

Steps To Demarcate the Effects of Chromophore Aggregation and Planarization in Poly(phenyleneethynylene)s. 1. Rotationally Interrupted Conjugation in the Excited States of 1,4-Bis(phenylethynyl)benzene

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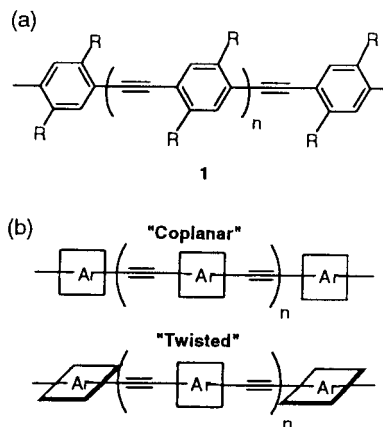
Received November 14, 2000

Abstract: A series of photophysical measurements and semiempirical calculations were carried out with 1,4-bis(phenylethynyl)benzene in search of evidence on the effects of phenyl group rotation and chromophore aggregation of oligo- and poly(phenyleneethynylene)s. It is suggested that planarization gives rise to relatively modest shifts of ca. 20–30 nm, which preserve the vibronic structure of the monomer and retain a high emission quantum yield. In contrast, it is proposed that aggregation gives rise to larger shifts and loss of vibronic structure.

1. Introduction

Organic compounds with aromatic groups that are linearly conjugated through acetylene linkages have been the center of much attention in the past few years^{1,2} (Scheme 1). Examples include relatively simple organic and metallo-organic chromophores,^{3,4} complex nanometer-scale molecular architectures,^{2,5} and high-molecular-weight conducting polymers such as poly(phenyleneethynylenes) (**1**, Scheme 1a). Interest in these compounds is derived primarily from their potential in a wide variety of applications^{6,7} where efficient charge transport, fast energy transfer, and good luminescence properties are required.⁸

Scheme 1



One of the most appealing attributes of poly(arylacetylenes) comes from the efficient electronic communication that occurs along their linearly conjugated structures. This effect can be attributed, at least in part, to the cylindrical symmetry of the triple bond, which is able to maintain conjugation between adjacent phenyl groups regardless of the relative orientations of their aromatic planes. One interesting manifestation of this structural trait comes from the relatively free rotation about alkyne–aryl single bonds,⁹ which leads to the coexistence and rapid equilibration of coplanar and twisted structures such as those illustrated in Scheme 1b. While equilibration may have no consequences in the ground state, changes in bond order upon electronic excitation or electron injection may lead to different properties for the coplanar and twisted structures of

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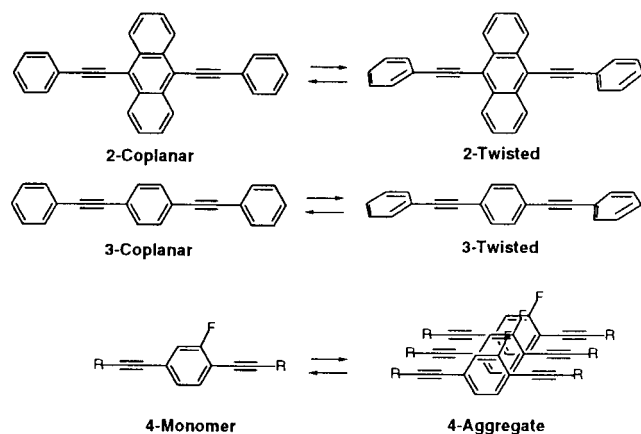
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Scheme 2



excited states and radical anions. For instance, it may be expected that substantial changes in the rotational profiles of the alkyne–arene single bonds occurring upon electronic excitation will be manifested in terms of spectral shifts in absorption and emission. In reality, while spectral changes are commonly observed as a function of concentration, fluidity, and phase transitions, they are generally interpreted in terms of excimer formation or excitonic coupling arising from cofacial aggregation.¹⁰ The first interpretation of spectral changes in terms of aryl group twisting and planarization¹¹ was offered by Bunz et al. while addressing the thermochromicity of alkyl-substituted polymers such as **1** (Scheme 1, R = C₁₀H₂₃).¹² Shortly thereafter, Levitus and Garcia-Garibay showed that planarization of monomeric 9,10-bis(phenylethynyl)anthracene **2** (Scheme 2), induced at low temperatures in stretched polyethylene films, resulted in significant changes on the UV absorption spectrum.¹³ At about the same time, using self-assembled monolayers and liquid crystalline phases to facilitate and organize cofacial dipolar interactions,^{10a,14} Swager and co-workers elegantly demonstrated the effects of aggregation on the photophysics of poly(phenyleneethynylene) self-assembled monolayers and alkyne-based mesogens.

While it is possible that most examples of spectral shifts reported in the literature involve planarization and aggregation, their relative contributions have remained a matter of speculation. In a recently submitted paper, we analyzed an example that illustrates the effect of chromophore aggregation without planarization. We report that both high concentration and crystallization of 2-fluoro-1,4-diethynylbenzene (**4**, R = C(Me)₂OH) result in spectral broadening and a red shift of 50–80 nm in the fluorescence emission.¹⁵ With only one phenyl ring, spectral changes in compound **4** should depend only on

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the effect of aggregation. In this paper we analyze the effect of phenyl rotation and aggregation on the absorption and emission properties of 1,4-bis(phenylethynyl)benzene **3** (Scheme 2). Using absorption, emission, and lifetime measurements in solution, low-temperature glasses, and stretched polyethylene films, we document the different spectral properties of coplanar and twisted conformations of **3** and compare those with the spectra of aggregates in the crystal. Spectral assignments are supported by semiempirical calculations of the ground-state rotational potential determined with the AM1 Hamiltonian, and by excited-state calculations as a function of interplanar angle carried out with the ZINDO/S method.

2. Experimental Section

2.1. Materials. 1,4-Bis(phenylethynyl)benzene **3** was purchased from Aldrich and purified by chromatography and recrystallization prior to use. Chloroform, ethanol, cyclohexane, and methylcyclohexane were obtained from Aldrich Chemical Co. in either HPLC or spectroscopic grade.

2.2. UV–Vis and Steady-State Fluorescence. Absorption spectra were recorded with either a Hewlett-Packard or a Shimadzu 3101-PC UV–vis–NIR spectrometer. Fluorescence and phosphorescence spectra were recorded in a Spex-Fluorolog II spectrometer equipped with an R 928 PMT detector and a 1943D phosphorimeter and were corrected for nonlinear detector response. Quantum yields were determined by using 1.0 N quinine sulfate ($\Phi_F = 0.546$) as a standard. Phosphorescence spectra were obtained in methylcyclohexane glasses at 77 K. Fluorescence signals were avoided by using a 40 μ s delay after the 10 μ s pulse from a xenon lamp. Decay curves were measured point-by-point by changing the delay in 10–50 μ s steps. Up to 100 pulses per point were accumulated, and 200 data points were typically collected per decay.

2.3. Time-Resolved Fluorescence. Fluorescence decays were measured with a time-correlated single-photon-counting fluorometer (Edinburgh Instruments, model FL900CDT) equipped with a pulsed H₂ discharge lamp operating at 0.4 bar (fwhm \sim 0.7 ns). Signal intensities were attenuated to detect photons at a rate of 1% of the excitation source repetition rate operating at 40 kHz. The instrumental response recorded with scattered light from a LUDOX suspension was used to deconvolute the short-lived fluorescence signals from the excitation pulse intensity profile. Measurements with solid samples and with amorphous glasses 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.

2.4. Semiempirical Calculations. The minimized ground-state energies and geometries for the all-planar and twisted conformations of compound **3** were calculated with the AM1 method.¹⁶ A representative portion of the ground-state rotational potential was analyzed by maintaining two phenyl groups coplanar while constraining the dihedral angle formed by the third phenyl group at various 15° increments. The electronic spectrum, including the direction of the transition dipole moment and the oscillator strength of transitions in the UV–vis, was calculated with the ZINDO/S method as implemented in the Hyperchem package.¹⁷ The CI matrix was calculated with the lowest 201 single excited configurations.

2.5. Dichroic Spectroscopy. The orientation of the transition dipole moment of compound **3** was determined by the stretched polymer method. Samples of linear low-density poly(ethylene) (Sclairfilm SL-1, 4 mils) from DuPont Canada were extensively washed with chloroform prior to exposure to concentrated solutions of **3**. Films were stretched to about 4 times their original length prior to incorporation of the substrate. Crystalline residues and externally adsorbed samples were removed by exposing the film to nonswelling solvents such as ethanol. Dichroic spectra were measured with a Shimadzu 3101-PC UV–vis–NIR instrument equipped with a Glan-Taylor calcite polarizer

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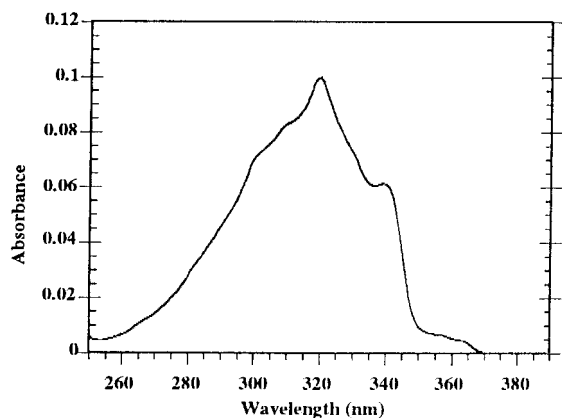


Figure 1. Lowest energy band in the UV spectrum of 1,4-bis(phenylethynyl)benzene in cyclohexane solutions.

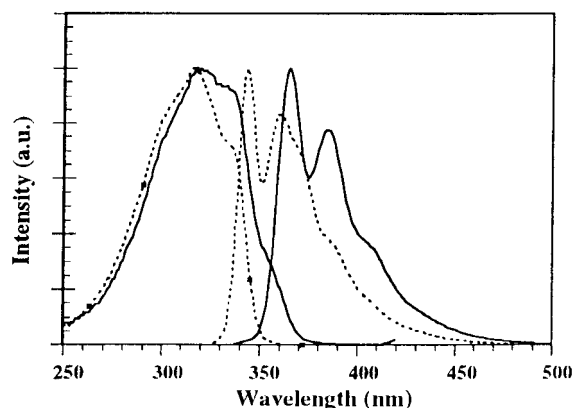


Figure 2. Fluorescence excitation (left) and emission of 1,4-bis(phenylethynyl)benzene in methylcyclohexane. The excitation spectra were collected by measuring the emission at $\lambda_{\text{ex}} = 350$ nm (dotted line) and $\lambda_{\text{ex}} = 480$ nm (solid line). The emission spectra were recorded by excitation at $\lambda_{\text{ex}} = 265$ nm (dotted line) and $\lambda_{\text{ex}} = 360$ nm (solid line).

in the sample beam. A detailed description of the method used in this work was published previously.¹³

3. Results and Discussion

3.1. Structural Heterogeneity by UV–Vis and Fluorescence Measurements in Solution. The lowest energy band in the absorption spectrum of **3** in cyclohexane solutions occurs between 250 and 370 nm with a λ_{max} at 320 nm and two shoulders at ca. 340 and 360 nm (Figure 1). Although the UV spectrum in Figure 1 appears homogeneous and samples used for measurements satisfied the highest purity tests, we were able to establish a strong spectral heterogeneity by fluorescence measurements in solution and in low-temperature glasses, and by absorption and emission spectra obtained in films of high-density polyethylene. As illustrated in Figure 2, fluorescence measurements carried out in dilute cyclohexane solutions with excitation at 265 or 360 nm produced emission spectra with similar vibrational resolution, but shifted by 23 nm from a λ_{max} of 341 nm to 364 nm at the 0–0 vibrational transition. Similarly, fluorescence excitation recorded by detection at 350 or 460 nm revealed spectral changes consistent with the presence of two or more absorbing species.

A systematic analysis of the excitation and emission of compound **3** was consistent with the presence of two or more species with different absorption and emission spectra. Excitation at the red edge of the absorption band at $\lambda_{\text{ex}} = 355$ nm results in a relatively clean red-shifted emission spectrum with

Table 1. Fluorescence Lifetimes of **3** in Cyclohexane Solutions at 298 K at Different Wavelengths

λ_{ex} (nm)	λ_{em} (nm)	τ (ns)	χ^2
280	370	0.74	0.890
280	400	0.79	0.910
280	450	0.89	0.825
320	400	0.96	0.822
320	450	0.97	1.084

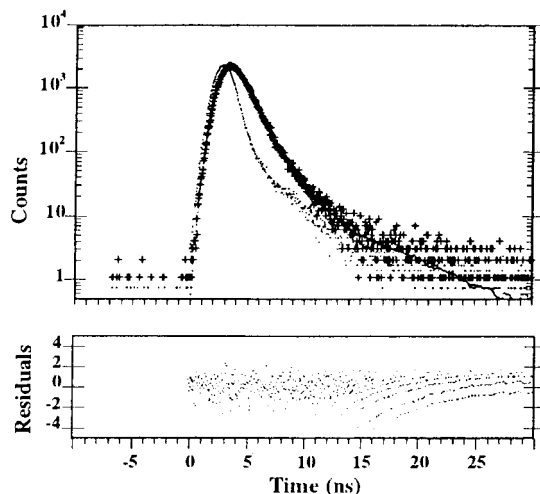


Figure 3. Fluorescence decay data for compound **3** in cyclohexane solution at 298 K by excitation at $\lambda_{\text{ex}} = 320$ nm and emission at $\lambda_{\text{em}} = 400$ nm. The instrument response (dots), decay data (crosses), and monoexponential fit (solid line) are plotted in the top frame. The residuals of the fit for a lifetime of $\tau = 0.96$ ns ($\chi^2 = 0.88$) are plotted in the bottom.

well-resolved vibrational bands at 364, 385, 409, and 436 nm (Figure 2, solid line). These correlate with a vibrational progression of 1500 cm^{-1} , which is associated with C–C stretching modes of the arylethynyl units in the ground state. By comparison, emission spectra obtained upon excitation at the blue edge of the absorption band at $\lambda_{\text{ex}} = 265$ nm revealed a blue-shifted spectrum with a vibronic progression that starts with bands at 342 and 358 nm, and a shoulder by 390 nm (Figure 2, dotted line). The emission of the blue-absorbing species reveals vibronic coupling with a C–C stretching mode that is similar to that observed in the red-absorbing species, with a progression of 1395 cm^{-1} . As discussed below, these frequency modes are satisfactorily reproduced by frequency calculations with the AM1 method.

Excitation between 250 and 380 nm resulted in systematic changes in the relative intensities of the two sets of bands shown in Figure 2, rather than a smooth displacement of the emission spectrum as a function of excitation wavelength. The observation of only two sets of bands is consistent with two spectroscopically distinguishable species rather than a continuum of structures. A fluorescence quantum yield of $\Phi_{\text{F}} = 0.91$ was determined for compound **3** by excitation at 320 nm in dilute cyclohexane solutions at 298 K. The same quantum yield was obtained in tetrahydrofuran solutions and by excitation at other wavelengths. These results indicate a very efficient radiative decay for all the major species absorbing at those wavelengths. Fluorescence lifetimes measured by time-correlated single photon counting upon excitation and detection at several wavelengths ranged from 0.74 to 0.97 ns (Table 1). Although decays were fit to single exponential functions due to the limited time resolution of our instrument (see Figure 3), they are likely to be more complex. However, a systematic trend suggests that the lifetime

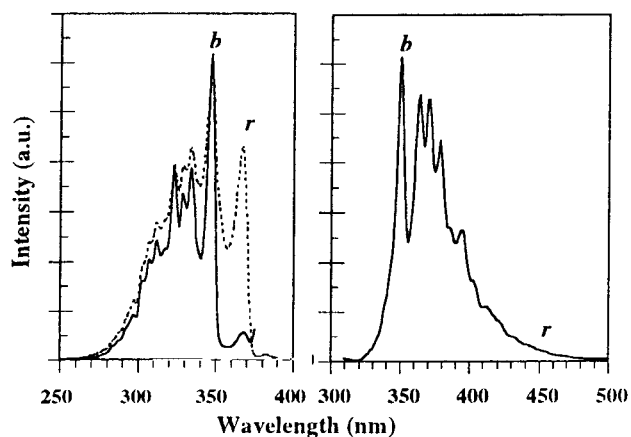


Figure 4. Fluorescence excitation (left) and emission spectra of 1,4-bis(phenylethynyl)benzene in methylcyclohexane obtained at 77 K. Wavelengths for excitation and detection of the red-shifted ($\lambda_{\text{ex}} = 550$ nm, $\lambda_{\text{em}} = 550$ nm) and blue-shifted species are indicated in the spectrum with “r” and “b”, respectively.

of the red-emitting species may be slightly longer than that of the species emitting in the blue.

3.2. Fluorescence of 3 in a Frozen Matrix at 77K. The subnanosecond singlet lifetimes of **3** are within the dynamic range experienced by molecular motions in fluid solutions at ambient temperature. The strong wavelength dependence and short excited-state lifetimes of compound **3** suggest that emission may originate from excited states that are not able to reach equilibrium within their lifetimes. Our attempts to measure the expected time evolution of the fluorescence spectra by time-resolved spectroscopy were not successful due to the limited time resolution of our instrument. However, to test this idea and to obtain more information on the spectra of the two distinguishable species, we determined the excitation and emission of **3** in methylcyclohexane glasses at 77 K, under conditions where most molecular motions should be frozen. Excitation scans were carried out by detection at the blue edge ($\lambda = 350$ nm) and the red edge ($\lambda = 450$ nm) of the emission spectrum. These gave rise to well-resolved spectra with strong 0–0 bands shifted by about 20 nm from each other, which are labeled “b” and “r” (for “blue” and “red”) in Figure 4. The emission spectrum obtained upon excitation at 320 nm is shown in the right frame of the figure. The large increase in the resolution of the excitation spectra at 77 K is particularly noteworthy. While results at ambient temperature had established two emitting species with their spectra shifted from each other by 22 nm (Figure 2), the absorption and excitation spectra at ambient temperature are broad and lacking structure (Figures 1 and 2). The high resolution of the excitation spectrum at 77 K supports a model where there may be a large number of absorbing structures in a dilute fluid at ambient temperatures, but where there are only two distinguishable absorbers upon freezing the sample in a rigid medium. Key to this interpretation is the assignment of the red and blue species to coplanar and twisted structures possessing different interaromatic rotational angles. As discussed below, the blue species is assigned to twisted structures, and the red one is assigned to coplanar 1,4-bis(phenylethynyl)benzene **3**.

3.3. Semiempirical Calculations. It is well known that the rotation of groups attached to triple bonds is essentially frictionless in the ground state.⁹ In the case of acetylenes, the cylindrical symmetry of the π -system allows for the rotationally uninterrupted conjugation of aromatic groups attached at the two ends of the triple bond. To test whether changes in the

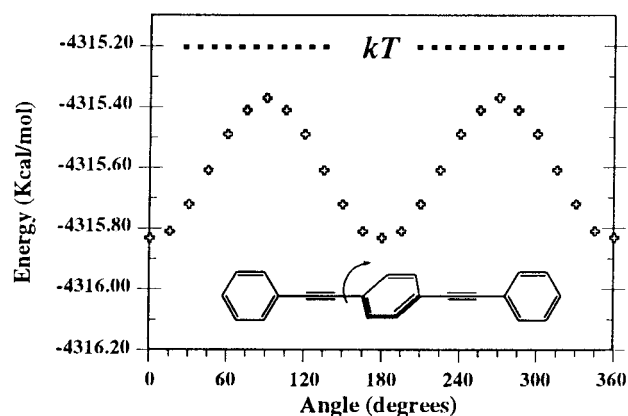


Figure 5. Ground-state rotational potential for the central phenyl ring in compound **3** calculated with the AM1 method. The thermal energy at 300 K is indicated with a dotted line.

absorption and emission spectra originate from structures with different angles between their interaromatic planes, we carried out a series of conformational and excited-state semiempirical quantum mechanical calculations. A representative portion of the ground-state rotational profile of **3** was calculated with the semiempirical AM1 Hamiltonian by maintaining the two external phenyl groups coplanar while constraining the dihedral angle formed by the plane of the central phenyl group to various increments of 15°. As expected, rotation of the central ring revealed a very shallow potential with a fully planar energy minimum that is only 0.5 kcal/mol below the perpendicular transition state (Figure 5). The calculated energy minimum is in good agreement with the X-ray structure of **3**, which was recently reported by Li et al.¹⁸

Although smaller energy changes were observed when only one of the external phenyl groups was twisted, no additional minima were observed. Frequency calculations confirmed that perpendicular conformations correspond to transition states for rotation about the triple bonds. The structure with one of the external rings in a perpendicular position contains a single imaginary frequency corresponding to its torsional motion about the alkyne–phenyl single bond. The structure with the central ring in a perpendicular position with respect to the outer two possesses two imaginary frequencies that correspond to rotation of the two external rings in either the same or opposite directions. Frequency calculations also suggest that modes near 1500 and 1395 cm^{-1} , which are responsible for vibronic coupling in the emission spectra, are associated with phenyl and alkyne C–C stretching modes along the long molecular axis.

It is expected from ground-state calculations that the instantaneous angle of rotation between phenyl groups in the ground state at ambient temperatures will be determined by their moments of inertia and by friction with the medium. However, while it is expected that all possible rotamers will be represented in the ground state, the wavelength dependence of the absorption and emission spectra must be determined by the energetics of the excited-state potential. The first indications of this effect can be obtained by molecular orbital analyses of the planar and twisted conformations of compound **3**. The main clues come from the extent of frontier orbital delocalization as a function of rotational angle, and from the changes in bonding and antibonding interactions between the atomic orbitals that constitute the σ -bonds connecting the phenyl and acetylene groups (Figure 6).

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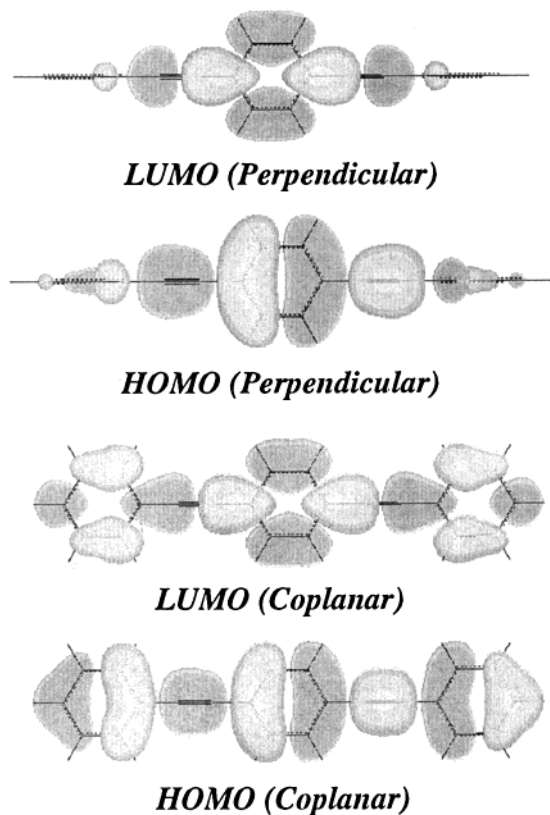


Figure 6. Frontier orbital representations for the twisted (top) and planar (bottom) structures of compound **3**. Notice that the twisted conformation is not an energy minimum.

The electronic properties and frontier orbital delocalization in coplanar and twisted conformations of diarylalkynes were recently analyzed by Seminario and Tour in the case of tolane (1,2-diphenylacetylene).¹⁹ Similar effects can be observed in the case of **3**, where the HOMO and LUMO of the twisted and planar conformations extend to varying degrees over the nuclear frame. The importance of phenyl group rotation in the excited state is also suggested by the changes in bonding interactions that are expected upon electronic excitation. While single bonds between alkyne and phenyl groups are expected in the ground state for all rotational angles, occupation of the LUMO in the excited state is expected to influence the bond order differently in the planar and perpendicular structures. The LUMO of the planar structure is delocalized over the entire molecule and gives a cumulene-type bonding pattern between the three phenyl groups. In contrast, the LUMO of the perpendicular structure resembles the LUMO of a diethynylbenzene, suggesting a more localized excited state. Given these differences, it is reasonable that rotation about the phenyl–alkyne bond should undergo important energetic changes while going from the ground state to the excited state.

As a test of our reasoning, we carried out semiempirical calculations of the electronic spectra and vertical transitions for each of the ground-state conformations previously optimized with the AM1 method. Single-point calculations were computed with the ZINDO/S method. The CI matrix was computed with the lowest 201 single excited-state configurations, and the vertical excitation energies obtained were added to the ground-state potential in Figure 6 to build the excited-state rotational

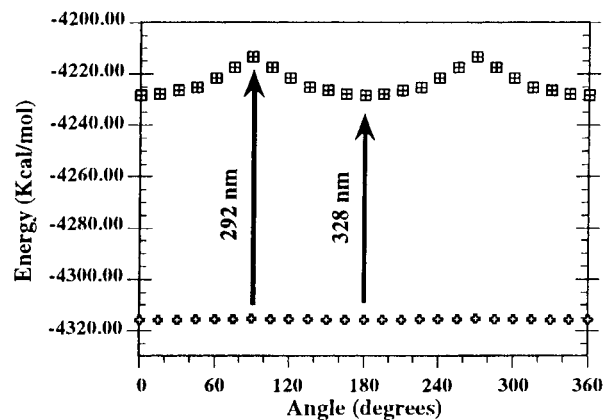


Figure 7. Rotational potential of 1,4-bis(phenylethynyl)benzene **3** in the ground state (AM1) and in the first excited singlet state. Transition energies were calculated with the ZINDO/S method. The wavelengths for vertical transitions in the planar and twisted conformations are indicated with labeled arrows.

profile shown in Figure 7. The ZINDO/S calculations overestimate the energy of the transition and predict a maximum shift of 36 nm as the structure of compound **3** changes from a coplanar conformation to one where the central phenyl ring is perpendicular to the other two. While qualitatively correct, this result is only in fair agreement with the experimentally observed shift of 22 nm. The ZINDO/S calculations also predict that the excited-state rotational energies increase sharply at angles that are close to the perpendicular transition state and that they are relatively shallow near the energy minimum. Calculations predict that the magnitude of the transition dipole moment is larger for the planar structure than for the twisted one, and that all of the lowest energy transitions lie along the long axis of the molecule. Some of these predictions can be tested experimentally by carrying out dichroic measurements using the stretched polyethylene film method.²⁰

3.4. Planarization and Dichroism of 3 in Polyethylene Films. The stretched film method is used to prepare dichroic samples with chromophores macroscopically aligned along the stretching direction.²⁰ It is well known that the main location of guest molecules is at the interface of amorphous and crystalline regions, and that stretching has the effect of aligning both the polymer chains of the matrix and the molecules absorbed therein. The main purpose of the polymer film method is to determine the orientation of the absorption transition dipole moments. However, it is also known that stretched polymers films can induce local micromorphological changes, including a reduction of the average free molar volume.²¹ The selection of certain guest structures upon applied stress in polyethylene films has been documented in poly(phenylenevinylene)s.²²

Results obtained with compound **3** are consistent with strong dichroism and planarization (Figures 8 and 9). The incorporation of compound **3** in a polyethylene film proceeded with efficiency from concentrated chloroform solutions. The dichroic UV absorption spectrum obtained with films stretched to about 4 times their original length is shown in Figure 8. The spectrum obtained with the polarizer axis parallel to the stretching

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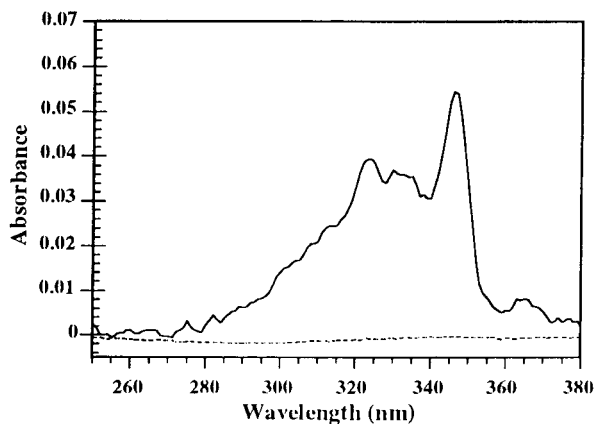


Figure 8. Dichroic UV spectra of 1,4-bis(phenylethynyl)benzene in a stretched polyethylene film. Dotted line: E_Y spectrum measured with the polarizer axis perpendicular to the stretching direction. Solid line: E_Z spectrum measured with the polarizer axis parallel to the stretching direction.

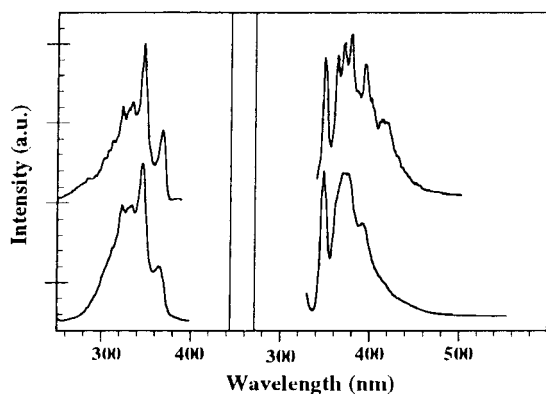


Figure 9. Fluorescence excitation (left) and emission (right) spectra of 1,4-bis(phenylethynyl)benzene **3** in polyethylene films at 298 K (bottom) and at 77 K (top). The excitation spectra were collected by measuring the emission at $\lambda_{em} = 360$ nm, and the emission spectra were recorded by excitation at $\lambda_{ex} = 300$ nm.

direction is shown with a solid line, and the spectrum obtained with the polarizer rotated by 90° is shown with a dotted line. The dichroic ratio, E_Z/E_Y , which is given by the intensity of the absorption along the two directions, indicates a nearly constant polarization along the entire band and is suggestive of a pure transition. The dichroic spectrum reveals very high orientation factors ($K_Z \approx 1.0$ and $K_Z \approx 0.0$), which indicate a nearly ideal alignment of molecules having their long axis along the stretching direction, as expected from the rigid rodlike structure of compound **3** and from the direction of the calculated transition dipole moment. Furthermore, the fluorescence excitation and emission obtained with **3** in polyethylene films at ambient temperature and at 77 K are also consistent with a high degree of planarization (Figure 9). The resolution and intensity of red edge absorption bands are significantly higher than those observed in solution (see Figures 1 and 2). A further increase in the population of the lower energy coplanar rotamers was also observed by the increased resolution upon lowering the temperature from 298 to 77 K. The excellent agreement between the absorption and fluorescence excitation spectra in the polymer film is also an indication of increased structural and dynamical homogeneity.

3.5. Aggregation in the Crystalline Solid State. The effect of cofacial aggregation on the photophysics of **3** has been documented by Li et al.¹⁸ by comparing results from measurements carried out in solution, doped in high concentration in

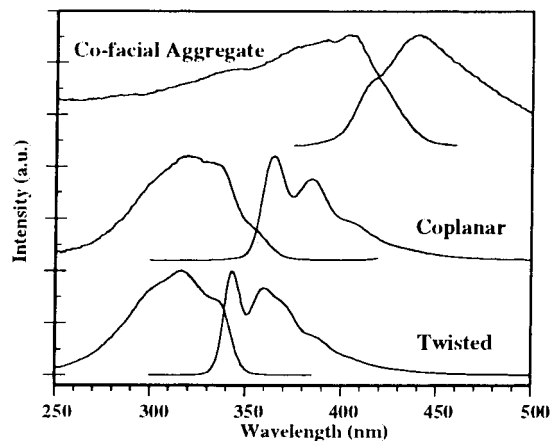


Figure 10. Excitation and emission spectra of samples of **3** obtained in solution and in the crystalline solid state. Proposed structural assignments, as illustrated in Scheme 3, are indicated next to each pair of spectra. The excitation spectra were acquired, from top to bottom, by detecting the emission at $\lambda_{em} = 350$, 350, and 265 nm. The corresponding emission spectra were obtained with excitation wavelengths at $\lambda_{ex} = 360$, 360, and 265 nm.

polystyrene films, and in the crystalline solid state. It was shown that compound **3** crystallizes in a planar conformation with close cofacial contacts of 3.48 \AA between aryl and acetylene groups of adjacent molecules.¹⁸ Measurements carried out by us in the solid state are illustrated in Figure 10 (top). Spectra assigned to the coplanar and perpendicular monomer structures, obtained in cyclohexane by excitation at the red (middle spectrum) and blue edges (bottom spectrum) of the absorption spectrum, are also included for comparison. In agreement with the findings of Li et al., the excitation and emission spectra of the crystalline aggregates are red-shifted by ca. 70–80 nm with respect to the spectra obtained in dilute solutions. As in previous literature reports, it was also found that crystalline aggregates display a significant loss of vibrational resolution.²³ Finally, it should be noted that a strong overlap between excitation and emission bands may be responsible for some distortion on the blue edge of the emission as a result of self-absorption.

3.6. Concentration Effects in Solution: Aggregation-Induced Planarization. A significant redistribution of vibrational intensities observed as a function of concentration in THF solutions ranging between 10^{-7} and 10^{-2} M was assigned by Li et al. to chromophore aggregation. Similar measurements carried out by us were shown to present a strong wavelength dependence, such as those illustrated in Figures 2 and 4. While there is no doubt that an increase in concentration should increase the population of aggregated species, we suggest that the spectral changes reported by Li et al. are due to *aggregation-induced planarization* rather than formation of observable cofacial excimers or excitonic interactions. As illustrated in Scheme 3, we propose that relatively disordered aggregates may lead to planarization of the phenyleneethynylene moieties long before a structurally demanding and spectroscopically observable cofacial interaction may occur. We noticed that the wavelength dependence of **3** remains unchanged in different solvents, over a wide concentration range, and at very low concentrations ($<10^{-7}$ M). We suggest that spectroscopically observable cofacial interactions in solution should be similar to those observed in the solid state and should require a more ordered aggregation than that attained in concentrated THF solutions.²³

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Scheme 3

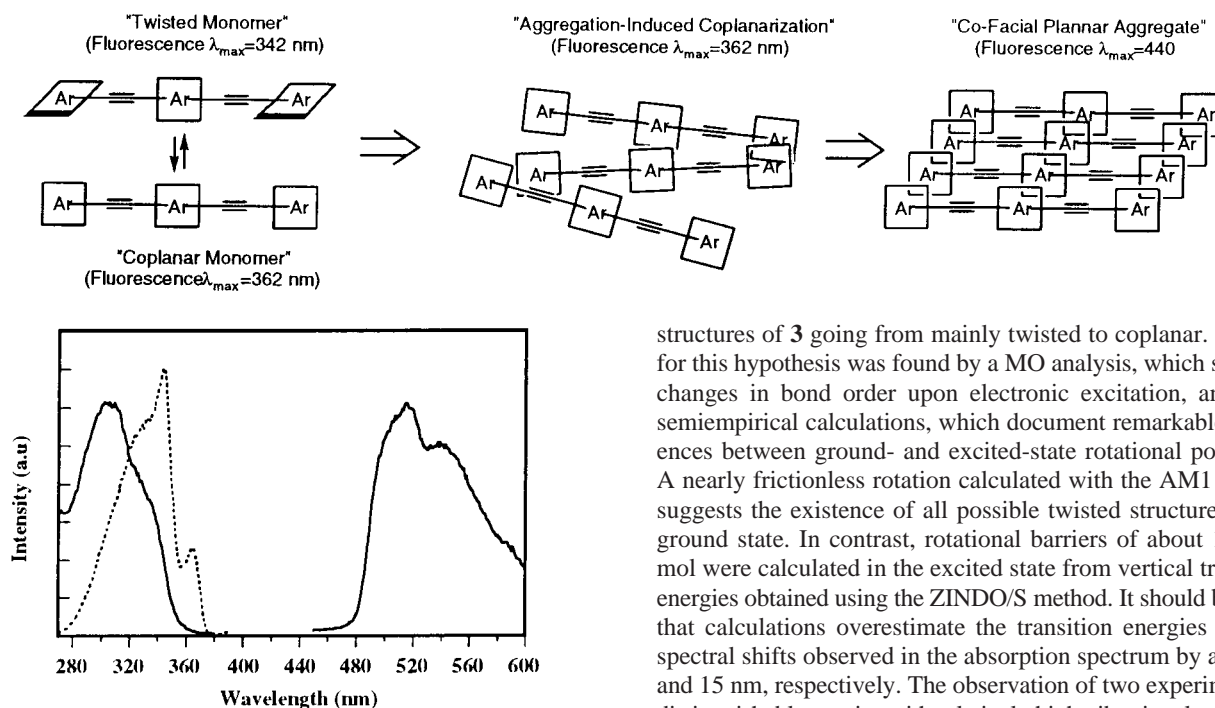


Figure 11. Phosphorescence excitation and emission spectra of samples of **3** detected at $\lambda_{em} = 550$ nm and excited at $\lambda_{ex} = 320$ nm in methylcyclohexane at 77 K are assigned to the perpendicular structures (full line). The fluorescence excitation spectrum obtained at 77 K by detection at $\lambda_{em} = 400$ nm (dashed line) is assigned mainly to the coplanar structure and is also shown by comparison (spectra shown in this figure were obtained with large slit widths and are of lower resolution).

3.7. Phosphorescence. Recent interest in triplet-state photo-physics properties of poly(phenyleneethynylene)s has been motivated by expectations of higher excited-state yields upon electron-hole recombination in electroluminescence applications. Although fluorescence yields at ambient temperature suggest a very weak emission, phosphorescence measurements were carried out with compound **3** at 77 K in dilute methylcyclohexane glasses. Accordingly, a relatively weak spectrum was obtained between 480 and 600 nm (Figure 11). The phosphorescence signal decayed in a relatively clean monoexponential fashion with a lifetime of 447 ms. Given that fluorescence measurements at 77 K had given strong indications of sample heterogeneity (Figure 4), we decided to explore the wavelength dependence of the phosphorescence emission and excitation spectra. Much to our surprise, neither the emission nor the excitation spectra displayed a significant wavelength dependence. Furthermore, the excitation spectrum of the phosphorescence signal is substantially blue-shifted, as expected for nonplanar rotamers. Although the observed phosphorescence signal may originate from an adventitious impurity, repeated sample purification gave reproducible results. We tentatively assign the triplet emission to the nonplanar structures which are vaguely analogous to phenylacetylenes and 1,4-diethynylbenzenes, both of which are known to display significant triplet yields and strong phosphorescence emission.^{15,24}

4. Conclusions

The wavelength dependence of the excitation and emission spectra of compound **3** requires the coexistence of (at least) two species with different UV absorption and emission properties. We suggest that red shifts of about 10–20 nm retaining a high degree of vibrational resolution may be assigned to

structures of **3** going from mainly twisted to coplanar. Support for this hypothesis was found by a MO analysis, which suggests changes in bond order upon electronic excitation, and from semiempirical calculations, which document remarkable differences between ground- and excited-state rotational potentials. A nearly frictionless rotation calculated with the AM1 method suggests the existence of all possible twisted structures in the ground state. In contrast, rotational barriers of about 15 kcal/mol were calculated in the excited state from vertical transition energies obtained using the ZINDO/S method. It should be noted that calculations overestimate the transition energies and the spectral shifts observed in the absorption spectrum by about 30 and 15 nm, respectively. The observation of two experimentally distinguishable species with relatively high vibrational resolution in both the absorption and emission spectra suggests that radiative transitions rely on coupled vibrations from species with nearly twisted and nearly coplanar structures. Our results also demand incomplete excited-state equilibration within the sub-nanosecond lifetime of 1,4-bis(ethynyl)benzene **3**. The planarization model was further supported by measurements carried out under conditions that affect the equilibrium and dynamics of the rotational structures, including low temperatures and rigid polyethylene films. High quantum yields of emission at ambient temperatures obtained upon excitation at several wavelengths indicate that radiative decay is efficient for the emissive species. Polarized absorption measurements in stretched polyethylene films indicate an almost perfect dichroism, as expected for a rigid rodlike molecule such as **3**. Fluorescence measurements in polyethylene films were also consistent with increased populations of the coplanar structures. Spectral changes in polyethylene as a function of temperature are particularly supportive of the planarization model. An alternative interpretation based on the coexistence of aggregate and monomeric species in a dynamic association-dissociation equilibrium under those conditions would be extremely unlikely. Measurements carried out with crystals indicate that cofacial aggregates having interaromatic distances of 3.48 Å give rise to severe line broadening along with spectral shifts as large as 70–80 nm. Studies in progress are aimed at exploring the generality of this effect in samples of substituted oligo(phenyleneethynylene)s, poly(phenyleneethynylene)s, and other aromatic chromophores.

Acknowledgment. We gratefully acknowledge the NSF for support of this work through Grants DMR998439 (MGG) and CHE9814118 (U.H.F.B.). U.H.F.B. is a Camille Dreyfus Teacher-Scholar (2000–2004). The authors also acknowledge Prof. Richard Weiss from Georgetown University for providing the polyethylene sample. JA003959V

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