

Polymorphs and Colors of Polydiacetylenes: A First Principles Study

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Abstract: Polydiacetylenes (PDAs) are exceptional polymeric materials with π -conjugated backbones. Several of them can undergo chromogenic transitions under a wide range of external stimuli. Herein we investigate the electronic structure and the resulting properties of model and experimental PDAs, by means of first principles condensed matter calculations. It is shown that torsional isomers with a twist of the lateral groups can be formed at small energetic costs. We also show the relationship that exists between these twists and the observed changes in the electronic and physical properties. In particular, the calculated changes in the absorption, Raman and NMR spectra agree with the color and property changes as observed experimentally. Therefore, these isomers are excellent models for the structures involved in the chromogenic transitions.

1. Introduction

One of the endeavors of nanotechnology is to develop smart materials that respond to changes in their surroundings, releasing for example an antitoxin when sensing a toxic chemical or a biological agent. A key issue for the design of such materials is to develop a universal nanometric transducer that can be tuned to convert a wide range of external stimuli (temperature, pressure, light, ion concentration, etc.) into an easily observable signal. Polydiacetylenes (PDAs) are particularly promising candidates for such universal devices as they are known, for well-chosen side groups, to undergo drastic optical absorption and fluorescence changes under applied stress,^{1,2} light exposure,³ heat exposure,^{4,5} change in chemical environment, or upon exposure to specific biochemicals.^{6,7} Furthermore, PDAs also show properties such as high third-order nonlinear susceptibility, and macroscopic exciton coherence length⁸ that render these compounds unique.

The topochemical solid-state polymerization of diacetylenes (DAs) to PDAs^{9–14} and the optical and electronic properties of PDAs^{15–18} have been extensively studied experimentally, but the underlying grounds for many of their exceptional properties are not fully understood. As in all quasi-one dimensional (1D) systems, electronic structures of PDA chains can be strongly affected by even relatively minor conformational changes. The main goal of this work is to contribute to the understanding of these electronic–structural relationships. To this end, a simple model PDA and a real PDA were studied.

PDA crystals and films, as well as gels and aggregates, exhibit several colors by which they are usually named, corresponding to different excitonic absorptions peaking at different wavelengths, λ_{\max} . The most frequent colors are “red” ($\lambda_{\max} \approx 540$ nm at room temperature) and “blue” ($\lambda_{\max} \approx 620$ nm). These are colors by transmission or diffuse reflection of samples containing small amounts of polymer. Other colors have been reported in the literature, for instance purple,^{19–23} suggesting

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that there are more than two electronic structures of PDA chains. Solutions of isolated chains are yellow, corresponding to limitation of the conjugation length by the continuous curvature of the chain's backbone.^{24–26}

λ_{\max} variations may be produced by variations of the van der Waals correction to the bare chain transition energy, by extension of the conjugation into the side group if a conjugated group is directly attached to the chain, or by elastic strain of the crystal, generally under uniaxial or hydrostatic stress. However, the large shift between blue and red colors should correspond to a change in the electronic configuration of the chain itself. A very important difference between the two classes is that blue chains are mostly not fluorescent, whereas red PDAs are fluorescent, often strongly at low temperature. This indicates that the “dark” excitons of A_g symmetry which are present in the optical gap of blue chains are shifted above the B_u exciton responsible for absorption and fluorescence; therefore, these states are even more affected than the B_u exciton itself.

The known structural facts related to colors of PDAs can be summarized as follows:

(i) All known blue PDA structures have well-characterized planar chains.^{13,15}

(ii) There are fewer reported “red” structures than “blue” ones. Among red PDAs, some structures have nonplanar chains,^{27,28} and some do not.^{29–32} The reported nonplanar chains correspond to cases where successive side groups are not translationally equivalent. Crystallographically, the “red” PDA poly(1,6-bis(diphenylamino)-2,4-hexadiyne) (poly-THD)²⁸ is of higher quality than the others, judging for instance by the number of collected reflections and the possibility of refinement with anisotropic thermal parameters.

(iii) In several PDAs showing a thermochromic transition, the high temperature red phase is less well ordered than the original blue one, but the blue phase recovered after a temperature cycle is less well ordered, too. However, the red structure is not disordered per se, for mainly two reasons: first, there is at least one reported good structure of a red PDA, poly-THD²⁸ with a nonplanar chain and no crystallographic evidence of disorder. Second, “reddish” and “bluish” disordered phases are known, and are universally referred to as “red” and “blue” in

the literature; examples of these are gels and cast films of poly(5,7-dodecadiyne-1,12-diol-bis(*n*-butoxycarbonylmethylurethane)) (poly-4BCMU) and poly(4,6-decadiyne-1,10-diol-bis(*n*-butoxycarbonylmethylurethane)) (poly-3BCMU).³³ Gels and cast films of the latter polymer absorb at the same wavelengths as the (partially polymerized) crystal, but the spectrum is strongly distorted, with an “exciton” line not more intense than a broad higher energy “vibron” band, whereas poly-4BCMU gels absorb at the same position as poly(5,7-dodecadiyne-1,12-diol bis[phenylcarbamate]) (poly-TCDU) crystals³⁴ (a standard red PDA), or annealed crystalline poly-4BCMU films. So, the differences in color are not related to disorder.

(iv) Taking into account the expected variations from material to material, published bond lengths in “red” PDAs are similar to the ones in “blue” polymers. So there is no experimental evidence that the difference between the two classes of PDAs is due to differences in bond lengths. The difference has to be found either in the chain conformation or in the effect of the side groups.

(v) Concerning the optical properties, at least two cases have been found where λ_{\max} is significantly lower than that of the “blue” phase and for which the chain is not planar: the completely polymerized poly-THD crystal²⁸ and a stable mixed bis(phenylglutarate) diacetylene (BPG)/poly-BPG crystal.²⁷ In both cases, optical absorption and electro-absorption³⁵ have shown that the chains are highly regular and behave as high-quality quantum wires, showing that their properties are not affected by disorder. In particular, the origin lines of absorption and luminescence spectra are almost coincident in energy.^{36,37} In the other cases, the repeat units are equivalent, and the chain is found planar.

This leads to an odd situation where chains having nearly identical geometries (all “blue” PDAs and the planar “red” ones) have different electronic structures, vibrational frequencies and ¹³C chemical shifts, while the properties of all (planar and nonplanar) red chains are very similar although their geometries differ. Therefore, concerning possible structural differences, the most likely ones are in bond angles, since experimentally, all C–C bond lengths are very similar.^{13,15}

So, it has been conjectured that “blue” structures are planar while “red” ones could be related to a twisted chain geometry,^{38,39} both with enyne arrangements and with very similar bond lengths. The twists in nonplanar “red” PDAs may not be observed if the side groups are nearly equivalent translationally because of technical difficulties:³⁹ detecting the nonplanarity of chains by diffraction might be difficult since it requires that all chain distortions in the crystal be “in phase”. Random phases would show up, apart from diffuse scattering, as distorted ellipsoids with anomalous shape and sizes. Unfortunately, this proposal cannot be tested based upon presently available diffraction data.

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Previous spectroscopic studies have shown that small stress-induced changes in in-plane angles only induce small and continuous variations (i.e., no phase change) in optical properties.^{40–42} On the other hand, in a nonplanar chain, different out-of-plane twist angles may generate significant differences in exciton energies and vibrational frequencies. The blue-versus-red dichotomy may therefore be less clear-cut than generally discussed in the literature. Indeed, several authors have observed a well-defined “purple” phase, a kinetic intermediate in the blue-to-red phase transition, with spectral properties intermediate between those of the blue phase and those of a red phase.^{20,21,43,44} Such findings suggest that a given material may be found in more than two states.

The idea that the electronic structure of conjugated chains may be affected by the side groups is not new.⁴⁵ In fact, substituents may have two kinds of effects on PDA chains:

(i) Electronic interactions between side groups and the chain. There have been numerous attempts to red-shift the optical absorption of PDAs by attaching conjugated rings directly to the chains, with only modest results (see among many ref 32). In most PDAs, including those studied here, side groups are attached to the chain via one or more $-CH_2-$ groups and, in these cases, the effects are invariably very small, as observed for instance for poly(1,6-bis(*N*-carbazolyl)-2,4-hexadiyne) (poly-DCH) that has $-CH_2-$ carbazole side groups and for which the optical absorption is only red-shifted by about 100 meV by comparison with the most frequent value.⁴⁶

(ii) Mechanical interactions. Most of the atoms in the unit cell belong to side groups, and minimizing their packing energy will be an important part of the total minimization leading to (perhaps locally) stable structures, even if this implies a cost in the chain energy itself. Hence, the possibility exists for different chain conformers. In order to model these effects, complete calculations similar to those performed in this contribution are obviously necessary.

A possible way of getting some information on the atomic structure of these polymers is to use *ab initio* modeling to complete and improve upon previous semiempirical approaches.⁴⁷ Unfortunately, these systems are often complex, with hundreds of atoms in the unit cell, have a long-range electronic conjugation in the direction of the polymer chain, and important van der Waals interchain interactions, which lead to time-consuming and complex calculations.

In this contribution, we use density functional theory (DFT), which makes possible the calculation of complex systems⁴⁸ at a limited computational cost, to model the behavior of PDA crystals. This allows considering all atoms of the crystal on an equal footing, in order to compute the interactions between side

groups and find the structures corresponding to local energy minima of the whole crystal in the electronic ground state.⁴⁹

We present first a simplified PDA model and we show that the color change can be associated with torsion isomers of the main polymer chain: the “blue” chain is almost flat with all of the side groups in the same plane and the “red” one has alternating twisted lateral groups. We show that these isomers reproduce well the experimental properties such as color, Raman frequencies, and ¹³C NMR chemical shifts. The electronic structures of the isomers are also presented. These materials are direct gap semiconductors with a variable band gap and some unusual twisted structures of the π -system. Knowledge of the electronic structure leads to a better understanding of the relationship between structure and properties and suggests the existence of colors for PDAs other than “red” and “blue”.

In the second part, we consider a real PDA: poly(1,6-bis(diphenylamino)-2,4-hexadiyne) (poly-THD). This PDA is one of the few for which a crystal structure determination found nonplanar chains: successive repeat units of a chain are alternatively twisted by $\pm 14^\circ$ relative to the average plane.²⁸ At room temperature, poly-THD has the spectral properties (color and NMR) of a red PDA,^{50,51} but its exciton absorption is significantly red-shifted³⁷ by comparison with that of poly-TCDU or that of red isolated poly-3BCMU chains in 3BCMU crystals.⁵² Also, its Raman frequencies are lower than those of typical “red” PDAs. Still, it is strongly fluorescent at low temperature, which has been considered a typical property of “red” PDAs. Three possible conformers of poly-THD are found, and some of their electronic and spectroscopic (optical absorption, Raman, and NMR) properties are computed and assigned to possible red, purple, and blue phases.

2. Calculation Method

Periodic electronic structure calculations were performed using density functional theory (DFT) within the PBE⁵³ generalized gradient approximation (GGA) and projector augmented wave^{54,55} (PAW) method as implemented in the VASP code.^{56,57} The choice of the PBE-GGA functional allows to compute large systems with good accuracy⁵⁸ and has a limited computer cost. For conjugated polymers, PBE-GGA functional can lead to a slight overestimation of conjugation,⁵⁹ but the impact on our calculated structure should be of only a few $\text{kJ}\cdot\text{mol}^{-1}$ and should cancel out partially for energy comparisons between these similar systems.

A Γ -centered $1 \times 4 \times 1$ *k*-point mesh with a high *k*-point density in the direction of the conjugated polymer chain was used; a coarser mesh in that direction induces an important modification of both

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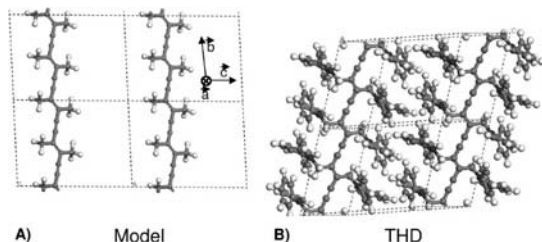


Figure 1. (A) Calculated crystal structure of a model polydiacetylene, poly(hexa-2,4-diyne). (B) Calculated structure of poly(1,6-bis(diphenylamino)-2,4-hexadiyne) (poly-THD).

the monomer and polymer structures.⁶⁰ A larger k -point sampling is not needed in the perpendicular direction as no dispersion of the electronic band structure is observed.

Two systems have been investigated: the first one is a model polydiacetylene, poly(hexa-2,4-diyne), with methyl groups as substituents and a large side-vacuum (8 Å) between repeated periodic images, so that a polymer chain has negligible interchain interactions (see Figure 1A). The second system is an experimentally known system,²⁸ poly-THD (see Figure 1B).

Computation of model poly(hexa-2,4-diyne) used a 450 eV cutoff, with only the atom positions being optimized (there was no residual stress in the polymer chain direction). Poly-THD was computed using a larger, 550 eV, cutoff (to account for the more electronegative nitrogen atoms) with both the atomic positions and the unit cell being optimized. For all systems, the residual forces on the atoms were lower than $0.01 \text{ eV} \cdot \text{Å}^{-1}$. The optimized geometries were ascertained as being local minima by vibrational analysis. Vibrational calculations were carried out by discrete calculation of the dynamical matrix followed by a diagonalization procedure to obtain the eigenvalues and eigenvectors. The vibration eigenvectors thus determined have components on all of the atoms in the unit cell, but some are mainly localized on specific atoms and can be assigned to a localized chemical bond vibration. In particular, some vibrations can be specifically associated with C=C and C≡C stretching modes. For the comparison between the experimental Raman active vibrations and the computed ones, a very precise calculation using a 700 eV cutoff was used for 166-THD to remove most of the possible basis artifacts.

NMR chemical shifts (within the implementation of Pickard et al.⁶¹) and absorption spectra were computed from an estimated dynamic dielectric constant using CASTEP.⁶² To correct for gap underestimation by DFT, a scissor operator of 1.0 eV was used in the absorption spectra calculations. Only band-to-band and not excitonic transitions are modeled. These absorption spectra give a qualitative description of the change in polymer color as a function of structural strain. Calculations were performed at 0 K, but room temperature vibrational entropy was reintroduced for some of the model calculations, to take temperature effects into account.

3. Conformational Study of a Model PDA: Poly(hexa-2,4-diyne)

The model PDA was built from hypothetical poly(hexa-2,4-diyne), with two monomer repeat units in the unit cell (see Figure 1A). Two types of isomerism are considered for this model as both methyl group rotation and torsion of the lateral substituents may exist. In this section, we will focus on the impact of these two isomerisms on total energy. The effects on

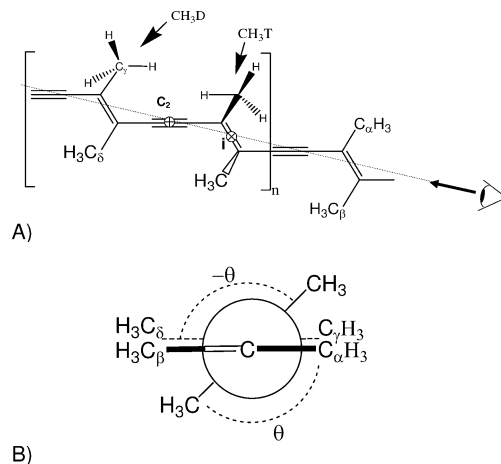


Figure 2. (A) Schematic representation of a model PDA: two possible rotamers $\text{CH}_{3\text{D}}$ and $\text{CH}_{3\text{T}}$ of the methyl groups are presented. The local inversion center i and the local rotation axis C_2 are shown. (B) View along the polymer backbone of a twisted model PDA showing the torsion angle θ . α , β , γ , and δ are carbon labels.

electronic structure and spectroscopic properties are discussed in sections 4 and 5.

3.1. Most Stable Structure of the Model PDA. The absolute minimum energy structure is found when the torsion angle between two consecutive methyl groups about a C≡C bond is 180° (see Figure 2); it follows that all of the carbons in this PDA are in the same plane. This structure is termed the flat model (**fm**). The optimal conformation of the CH_3 group is found for a C–H bond being in the molecular plane with an H pointing toward the double bond; this conformation is abbreviated $\text{CH}_{3\text{D}}$. In the $\text{CH}_{3\text{T}}$ conformation, a C–H bond is in the same plane but points toward the triple bond (see Figure 2A).

3.2. CH_3 Conformational Effect. The $\text{CH}_{3\text{T}}$ conformation is a transition state on the energy path of methyl rotation around the C–C bond, linking two consecutive $\text{CH}_{3\text{D}}$ states. For the **fm** structure, the calculated barrier for methyl rotation is about $2 \text{ kJ} \cdot \text{mol}^{-1}$. The change from a $\text{CH}_{3\text{D}}$ to a $\text{CH}_{3\text{T}}$ conformation induces a small increase in the C≡C bond length from 1.231 to 1.234 Å and an increase in the C=C length from 1.387 to 1.392 Å, concomitant with a decrease of the C–C length from 1.404 Å to 1.398 Å. Therefore, CH_3 conformation has a small (but larger than calculation noise) effect on the properties of the main polymer chain.

3.3. Torsion Effect. It was proposed that color isomerism in PDA chains is linked to planar/nonplanar conformational changes.^{18,38,39,63–65} Consequently, we next focused on rotation about the main polymer axis. This rotation is characterized by the dihedral angle θ between two CH_3 groups located on each side of a C≡C bond (see Figure 2B). The energy as a function of torsion (Figure 3) shows two minima located at $\theta = 0^\circ$ and $\theta = 180^\circ$. The $\theta = 0^\circ$ conformation is $5 \text{ kJ} \cdot \text{mol}^{-1}$ less stable than the $\theta = 180^\circ$ one. $\theta = 0^\circ$ corresponds to the isomer in which two methyl groups around a C≡C bond are on the same side (i.e., *cis* conformation) whereas $\theta = 180^\circ$ corresponds to a structure where all the methyl groups are *trans*. As only the *trans* structure has been observed experimentally, we shall focus on the $90^\circ \leq \theta \leq 180^\circ$ range in the next sections.

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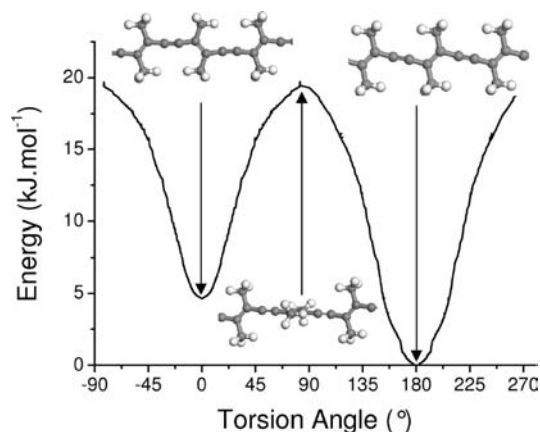


Figure 3. Energy change as a function of twist angle θ for the model PDA. Energy is referenced to that of **fm** ($\theta = 180^\circ$). The pathway linking the transition state to the minima was estimated using a damped dynamics from the transition-state structure. Residual forces on the atoms in all of the structures in this calculated pathway are weak and below $2 \times 10^{-2} \text{ eV} \cdot \text{\AA}^{-1}$.

The transition state (characterized by a vibrational analysis) for the rotation about the $\text{C}\equiv\text{C}$ bond for the $\text{CH}_{3\text{D}}$ conformation of the lateral methyl groups corresponds to a torsion angle of about 90° . As a result, CH_3 groups about a $\text{C}\equiv\text{C}$ bond are in perpendicular planes. We name this conformer the perpendicular model (**pm**) and will consider it as a limit structure for PDAs even if presently there is no proof that such a large torsion can be achieved experimentally in the solid state. The rotational energy barrier of $19.5 \text{ kJ} \cdot \text{mol}^{-1}$ is small. This barrier increases for a $\text{CH}_{3\text{T}}$ methyl conformation by 30% to $27 \text{ kJ} \cdot \text{mol}^{-1}$. This torsion barrier is low but is 1 order of magnitude larger than previous estimates obtained from semiempirical⁶⁶ and restricted Hartree–Fock⁶⁷ calculations ($1.2 \text{ kJ} \cdot \text{mol}^{-1}$), emphasizing the need for an *ab initio* approach including electronic correlation to solve this difficult problem. The zero-point energy and vibrational entropy can be estimated from vibration calculations, increasing at room temperature the free energy barrier to $21 \text{ kJ} \cdot \text{mol}^{-1}$. This energy is small in comparison with the energy of a typical $\text{C}-\text{C}$ bond ($350 \text{ kJ} \cdot \text{mol}^{-1}$), showing that torsion does not induce any bond breaking but rather a bond reorganization.

The **fm** and **pm** models show intermediate $\text{C}=\text{C}$ and $\text{C}-\text{C}$ bond lengths (see Table 1) between single and double bonds and close to aromatic ones (1.40 \AA). Nevertheless, these structures show some structural differences. Bond length changes could give hints on the degree of conjugation of the π -system over the polymer. A $\text{C}=\text{C}$ bond length closer to that of a typical double bond (ethylene type: 1.30 \AA) suggests a strong bond localization, whereas an increase toward an aromatic bond (1.40 \AA) is suggestive of strong conjugation. The **fm** structure has the longest $\text{C}=\text{C}$ bond, while the **pm** has the shortest one, indicative of the weakest conjugation. Nevertheless, the bond length in **pm** is longer than that found in butadiene, which supports partial conjugation over the polymer chain.

In all cases, for a real PDA with large interacting substituents, the torsion energy is always low enough for the total energy to be influenced or even dominated by steric effects of the interacting substituents. A steric contribution of only $5 \text{ kJ} \cdot \text{mol}^{-1}$

per lateral group is enough to overcome the barrier and to induce a strong torsion. In a real PDA, steric effects can be strong enough so that a twisted isomer can become a local minimum. A possible conformation isomer of the flat PDA could then be any nonplanar twisted PDA. The amount of twisting in the PDA should be controlled by the interactions between lateral chains.

In summary, we have shown that torsional isomers of PDAs can exist within a narrow energy range. We have studied only alternating torsion structures where the strain angles of successive units alternate in sign: $+\theta$ and $-\theta$. Nevertheless, a recent experiment has shown that some PDAs formed from *achiral* monomers become chiral upon polymerization⁶⁸ under polarized UV light. A way to achieve chirality from an achiral system is to induce a helix-like structure. This can be easily done within our model system by replacing the alternating $+\theta/-\theta$ torsion angle occurrence by a torsion of constant sign, leading to a helical chain.

3.4. Helical PDA. In our periodic calculations, the helix pitch has to be equal to the unit cell size. Thus, exploration of a helical PDA cannot be done for all possible torsion angles θ as for the previous alternating structures due to limitations in calculation size. With this in mind, we have modeled a six-monomer-chain helix with a torsion angle of nearly 120° , as shown in Figure 4. The geometrical parameters of the helix structure are intermediate between those of the **fm** and **pm** models, yet closer to those of the **pm** one (see Table 1). This helix structure is $13 \text{ kJ} \cdot \text{mol}^{-1}$ less stable than the **fm** structure, but $2 \text{ kJ} \cdot \text{mol}^{-1}$ more stable than the alternating structure with a $+120^\circ/-120^\circ$ configuration. Therefore, the formation of a helix is not energetically costly.

The structure seems to be dominated by only the local torsion of the lateral chains, and both alternating and helical model energies are very close and should be experimentally achievable. Torsion of the lateral groups has some effect on bond lengths, and this should translate into a modification of some physical properties. Next we focus on changes in some of the physical properties of the PDA with torsion angle.

4. Electronic Structure of PDA vs Torsion

As previous theoretical studies have predicted an effect of substituents on the band gaps of finite molecular PDAs,⁶⁹ we will first focus on the effects of substituent isomerism on the band gap of the model PDA.

4.1. Relationship between Band Gap and Isomerism. DFT underestimates band gaps. However, in most cases, it gives a good qualitative overview of the changes in the electronic structure since the relative order of energies is more reliable. Evolution of the DFT band gap at three k -points ($\Gamma(0,0,0)$, $M(0,0.25,0)$, $F(0,0.5,0)$) of the Brillouin zone as a function of torsion angle is shown in Figure 5. From 180° to 90° , the gap of the $\text{CH}_{3\text{D}}$ isomer is increased by a factor 4.5 as it changes from 0.6 to 2.7 eV . Around 110° , an inversion of the band structure is observed with the minimum band gap transferred from Γ to M and finally to F . The $\text{CH}_{3\text{T}}$ isomer behaves identically but shows lower band gaps by about 0.2 eV .

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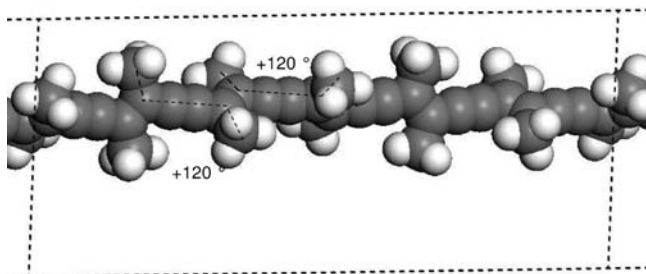
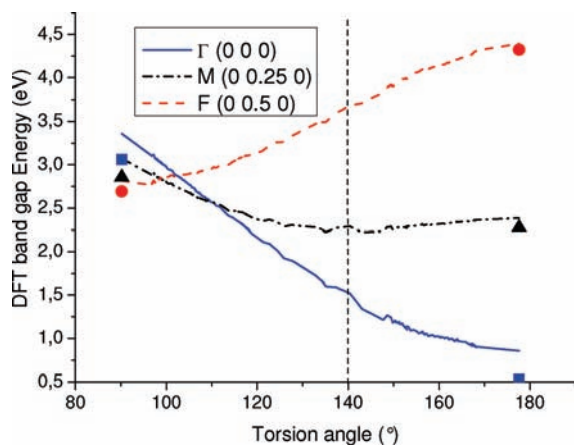
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Table 1. Comparison between Energies and Geometrical Parameters for the **pm**, **fm**, and **helix** Model Structures with CH_{3D} Methyl Conformation, the Calculated Poly-THD Polymorphs, and for Experimental Poly-THD^a

	θ (deg)	energy/monomer unit (kJ·mol ⁻¹)	C≡C (Å)	C=C (Å)	C–C (Å)
fm	180	0	1.231	1.387	1.404
pm	90	9.6	1.228	1.374	1.418
helix	119.2	6.5	1.228	1.377	1.414
176-THD	175.7	18	1.236	1.393	1.406
166-THD	166 (166)	0 (20)	1.237 (1.232)	1.396 (1.392)	1.404 (1.398)
114-THD	114 (135)	-7 (34)	1.231 (1.235)	1.381 (1.385)	1.416 (1.411)
exp	166	–	1.205	1.359	1.426

^a For the model PDA, the **fm** model is chosen as a reference, whereas for the poly-THDs, 166-THD is the reference. The re-optimized structures and energies in the experimental unit cell are given in parentheses.

**Figure 4.** Structure of a model helical PDA. Torsion angles are shown schematically.**Figure 5.** Changes in gap energy at different k -points of the Brillouin zone as a function of torsion angle θ . The lines are given for the CH_{3D} rotamer. The filled squares, triangles, and circles are for the CH_{3T} rotamer at respectively $\Gamma(0,0,0)$, $M(0,0.25,0)$, and $F(0,0.5,0)$ points for $\theta = 90^\circ$ and $\theta = 180^\circ$.

For a given torsion, isomerism between CH_{3D} and CH_{3T} has only a small effect on the electronic structure in comparison with torsion and cannot explain a drastic change in optical properties.

4.2. Evolution of the Band Structure as a Function of Chain Torsion. The computed band structures of **fm**(CH_{3D}) and **pm**(CH_{3D}) PDAs are presented in Figure 6. The **fm** band structure corresponds to a Γ -point direct gap semiconductor with a 0.6 eV DFT band gap. A strong dispersion of the highest occupied and lowest unoccupied bands (of about 2.6 eV) is observed. These bands correspond to the perpendicular π -system (π_\perp) that is antisymmetric with respect to the polymer plane as shown by the projected density in A.1 and A.2 of Figure 6. The large width of these bands is caused by the strong overlap of the 2p_x orbitals allowing for strong electronic conjugation. The second-highest filled band has a bandwidth half that of the π_\perp system. It corresponds to the parallel π system (π_\parallel) in the

plane of the polymer which is dominated by the 2p_z orbitals involved in the C≡C bonds. The band is narrow as the 2p_z orbitals of the carbons of the C=C bonds are also involved in the σ C–CH₃ bonds and can only interact weakly with the ones of the C≡C bond. In **fm**, the π_\parallel and π_\perp systems are disconnected as expected from symmetry.

The band structure of a 90° twisted **pm** PDA corresponds to a F(0,0.5,0)-point direct band gap semiconductor, with a minimal gap of 2.75 eV. The bandwidth of the π -systems is reduced to 0.5 eV. The density projection on the highest occupied bands (B.3 and B.4 in Figure 6) shows that the π -electrons cannot be separated into perpendicular and parallel systems: the resulting structure is a twisted π -structure as torsion allows some overlap between the π systems of two adjacent monomeric subunits, maintaining a partial conjugation.

Comparison of these very different electronic structures gives some insight into the origin of the low-energy torsion barrier between **fm** and **pm**: there is compensation, during torsion, between the loss of conjugation of the π_\perp that destabilizes the total energy, and the increase of the conjugation of π_\parallel that stabilizes it. Transformation from **fm** to **pm** bears some similarity with the transition from normal aromaticity to Möbius aromaticity.⁷⁰

PDAs happen to be direct gap semiconductors whatever the torsion, with the gap tuned by the geometry of the side groups. Furthermore, the strong change with torsion of the electronic structure should modify the observed properties: **fm** should absorb low-energy photons, whereas **pm** should absorb higher-energy ones. PDAs are known to possess different isomers with different colors and spectroscopic properties. One is a blue phase (absorbing low-energy red photons), and the other is a red phase (absorbing high-energy blue photons). The different phases of PDAs could correspond to a torsion isomerism that modifies the electronic structure and also the color. In order to check this hypothesis, we investigated next some spectroscopic properties of these isomers.

5. Changes in Spectroscopic Properties with Torsion

5.1. Optical Absorption. The computed energy bands correspond to free carriers, whereas the absorption spectra are those of excitons. However, the experimental exciton binding energies of blue and red PDAs are very similar,^{16,46} so the ordering of transition energies will be the same. The computed absorption spectra for the model PDA as a function of torsion angle are shown in Figure 7. Two families of structures are observed. The structures with a torsion angle above 140° show a strong absorption at longer wavelengths whereas the ones below 140°

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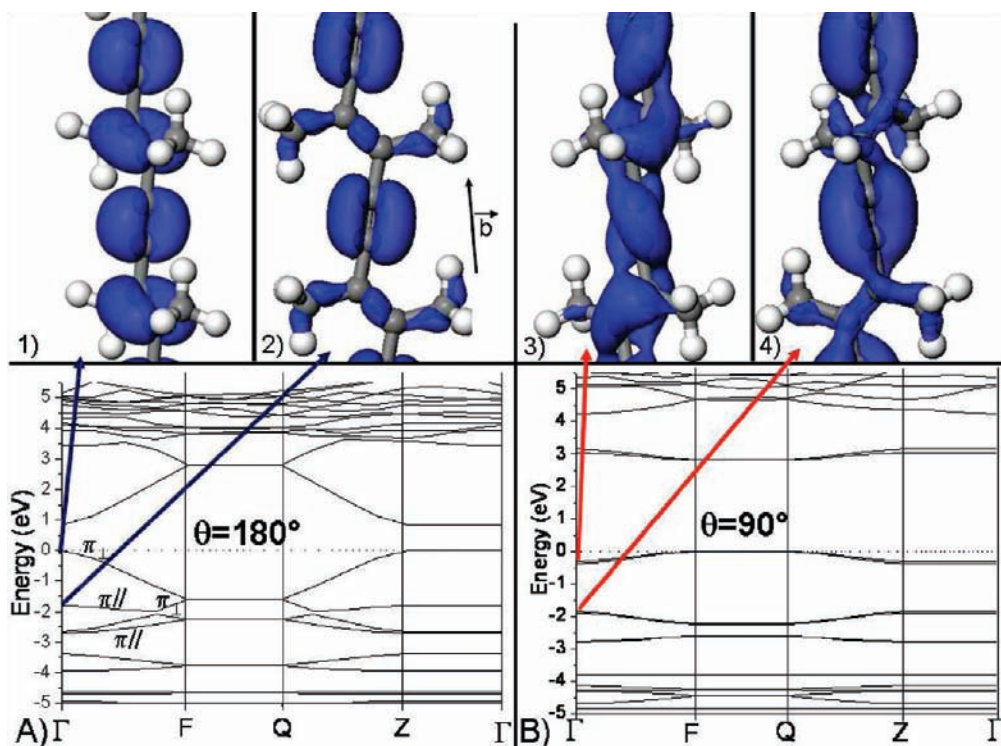


Figure 6. (A) Band structure of **fm** (CH_3D) ($\theta = 180^\circ$). The relative coordinates of the given k -points are: $\Gamma(0,0,0)$, $F(0,0.5,0)$, $Q(0,0.5,0.5)$, and $Z(0,0,0.5)$. π_{\parallel} and π_{\perp} denote the bands associated with the parallel and perpendicular π -systems, respectively. (1) Projected electronic density at Γ -point of the highest filled band (π_{\perp}) for **fm**. (2) Projected density at Γ -point of the second-highest filled band (π_{\parallel}) for **fm**. (B) Band structure for **pm** (CH_3D) ($\theta = 90^\circ$). (3) Projected electronic density at Γ -point of the highest filled band for **pm**. (4) Projected density at Γ -point of the third-highest filled band for **pm**.

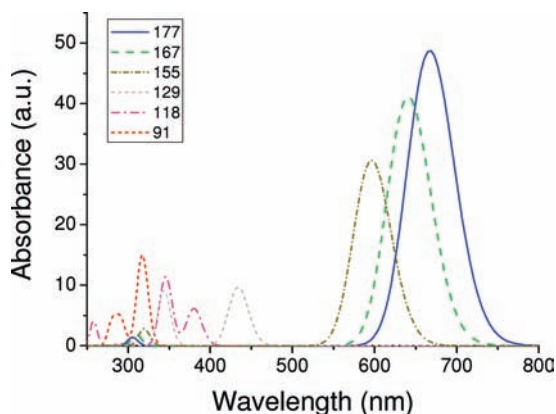


Figure 7. Calculated absorption spectrum of the model PDA as a function of torsion angle θ .

show absorptions at shorter wavelengths, consistent with the changes in gap energies discussed previously. The nearly flat structure should appear blue and the strongly twisted ones should appear red. For torsion angles in the range 120 – 160° , absorption spectra are intermediate between those of **fm** and those of **pm**, hinting that, in some PDAs, intermediate colors between red and blue could be encountered.

5.2. Vibrational Signature of Torsion in PDAs. Experimentally, Raman frequencies of $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ bonds are characteristic of “blue” and “red” forms: typical experimental $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}\equiv\text{C}}$ stretching frequencies are, for a “blue” phase, about 1460 and 2080 cm^{-1} , while those of a “red” phase are 1520 and 2120 cm^{-1} . DFT is known to give reliable vibration frequencies that can be used to investigate local bonding⁷¹ even

when all other properties are not as well reproduced.⁷² We have computed the effect of torsion on the vibrations of our model PDA.

Symmetry operations such as a b -glide plane, an inversion center and a C_2 rotation axis (see Figure 2) are conserved (or nearly conserved at least for the carbon chain). As a result, each $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ stretching mode is associated with two frequencies. These two frequencies can be labeled as symmetric or antisymmetric with respect to either the inversion center (for the $\text{C}\equiv\text{C}$ mode) or the C_2 rotation (for the $\text{C}=\text{C}$ mode). Because of the local inversion that exchanges the two $\text{C}\equiv\text{C}$ bonds in the unit cell, both $\text{C}\equiv\text{C}$ bonds are equivalent, and only the local symmetric $\text{C}\equiv\text{C}$ stretch is Raman active. For the $\text{C}=\text{C}$ stretch, only flat chains have a strict inversion center preventing the antisymmetric $\text{C}=\text{C}$ stretch from being Raman active. For nonplanar structures, this inversion center transforms into a C_2 axis. The associated symmetric mode has an A -symmetry and is Raman active. The antisymmetric mode has a B -symmetry and is also Raman active but is expected to be weaker. We next focus on symmetric stretching modes that should always be active and dominate the Raman spectra of PDAs for all torsions.

Figure 8 shows the variation of Raman active symmetric stretching frequencies as a function of torsion angle for two different isomers. Both $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ stretching frequencies increase with a decrease of the torsion angle (for both CH_3D and CH_3T conformers). The $\text{C}\equiv\text{C}$ frequency increases by 43 cm^{-1} for CH_3D and 53 cm^{-1} for CH_3T . The $\text{C}=\text{C}$ frequency

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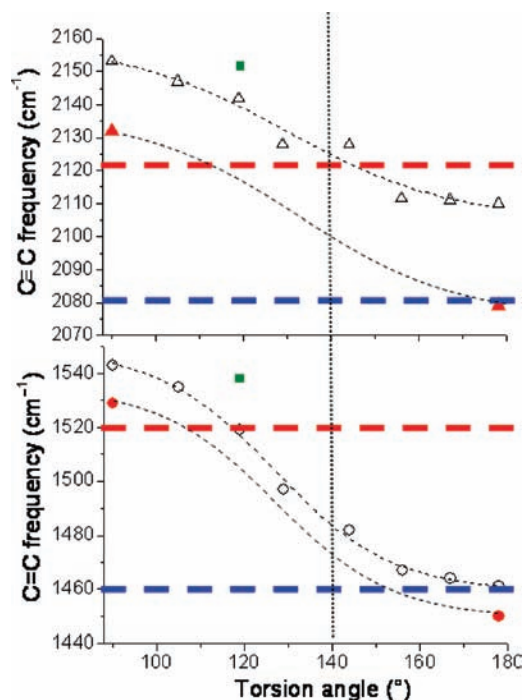


Figure 8. Computed symmetric C≡C and C=C stretching frequencies as a function of torsion angle θ . Open triangles and circles correspond respectively to the C≡C and C=C stretching frequencies of the CH_{3D} isomer of the twisted model. The filled triangles and circles are for the CH_{3T} isomer. The filled squares correspond to the helix structure. Typical experimental Raman frequencies for red PDAs (2120 and 1520 cm⁻¹) and blue PDAs (2080 and 1460 cm⁻¹) are shown as horizontal dashed lines.

increases by 82 cm⁻¹ for CH_{3D} and 79 cm⁻¹ for CH_{3T}. Thus, C=C and C≡C stretching frequencies are mostly sensitive to torsion and, for a smaller part, to methyl conformation. Conformation change from CH_{3T} to CH_{3D} induces a small shift of 10–30 cm⁻¹ to lower frequencies, whereas torsion induces a shift in the range 40–80 cm⁻¹. Frequency changes become bigger for angles below 140°: the change in the C=C stretching frequency between 140° and 180° is only 20 cm⁻¹, whereas it is 60 cm⁻¹ between 140° and 100°.

The frequency changes can be associated with electronic structure changes. Torsion toward 90° diminishes conjugation over the entire polymer chain, leading to a stronger bonding of the double and triple bonds (and a weaker one for the single bond). As a result of stronger bonding, the associated C=C and C≡C stretching frequencies increase. The same reasoning applies to CH_{3D} and CH_{3T} in a similar way to the well-known *E*–*Z* isomerism of 2-butene: the CH_{3D} conformer allows a better electronic conjugation over the methyl without secondary antibonding interactions between the C=C carbons and the methyl groups as it happens in CH_{3T}. A better electronic conjugation weakens the C=C and C≡C bonds, decreasing the associated frequencies. The helical model system exhibits C=C and C≡C stretching frequencies at 1538 and 2152 cm⁻¹, respectively, close to those of **pm** as expected from the structural study. The calculated shifts of the model PDA torsion isomers are similar to the experimental Raman shifts associated with a blue/red isomerism.

5.3. NMR Signature of the Torsion. The calculated ¹³C NMR chemical shifts for the C≡C bond are shown in Figure 9. The chemical shifts of the carbons increase with torsion angle between 90 and 180°. Two distinct behaviors appear: first there is a small change in chemical shielding of about 2 ppm (from

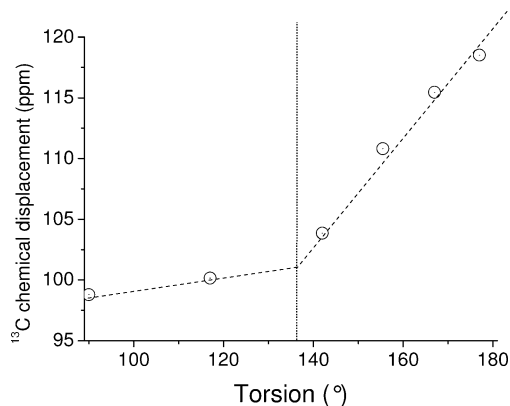


Figure 9. Calculated ¹³C chemical shifts for the C≡C carbons as a function of torsion angle θ .

98 to 100 ppm) between 90° and 140°, then a steep change occurs (17 ppm) between 140 and 180°. This change in chemical shift is associated with the change in electronic structure that was studied in the previous sections. The chemical shift becomes larger as electron conjugation over the polymer increases. The triple bond becomes more double bond-like as conjugation increases, leading to a shift toward C=C chemical shifts.

The calculated values for our simplified model are also consistent with experimental NMR results⁵ on blue/red PDA isomerism. Usually, the C≡C shift of a blue isomer is observed around 105–107 ppm and that of a red phase around 100–103 ppm, even if these values are just indications.

We have found using our model that the blue/red isomerism of PDAs may be linked to chain torsion. In this model, torsion is imposed in the calculation and is not a consequence of crystal packing and of the effect of substituents and interchain interactions which are present in real PDAs; the tilt angle is set by minimizing the total crystal energy, so in principle, the minimum energy may correspond to any tilt angle. Thus, the excited-state energy may lie in a fairly broad range, and indeed, values between 1.8 and 2.5 eV are observed. However, many known PDAs have exciton energies close to 1.9 or 2.4 eV at room temperature, small deviations from these values being possibly due to other causes listed above (see Introduction). All planar chains belong to the former group, but the situation in the latter is less clear as discussed in this work. One possible explanation of this clustering of exciton energies is the following: a very successful synthetic route for the preparation of reactive DA monomers has been the reaction of an isocyanate with a diynediol. This produces side groups bearing -(CONH)- moieties leading to H-bonding between neighboring monomers which fixes the intermolecular distances to about 4.9 Å, therefore meeting a major topochemical condition for reactivity. The resulting PDA chain has two 1D lines of H-bonds running parallel to it and separated from the chain by (-CH₂)_n spacers with $n = 1–9$ in known PDAs. This may contribute to enforce specific chain geometries (tilt angles), for instance if the alkyl chain is all-*trans* or contains a *gauche* bond.

It may be expected that other differently organized systems may lead to different, not previously observed PDA conformations.

Next, we investigate an experimentally synthesized PDA which has no H-bonds, a small tilt angle and an intermediate value of exciton energy, in order to check that the results obtained on our model can be transposed to a real-life system. To this end, interchain and interside groups' interactions are taken into account.

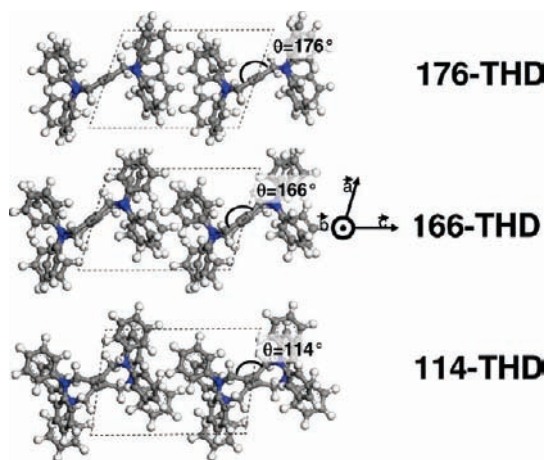


Figure 10. Calculated structures ($\theta = 176$, 166 , and 114°) of poly-THD. Dashed lines delineate the unit cell.

6. Study of an Experimental System: Poly-THD

Polymerizable DA monomer crystals always have larger side groups than our model compound, but the same approach can be applied to a real DA. In order to see if the same relationship between torsion and color can be established in a real system, the PDA known as poly(1,6-bis(diphenylamino)-2,4-hexadiyne) (poly-THD) was chosen (see Figure 1B). Its reflection spectrum,⁵⁰ ^{13}C NMR chemical shifts,^{63,73} and the observation of a strong low-temperature fluorescence are fully consistent with those of a red PDA.⁵¹ The polymer crystal structure is known, and it shows that the unit cell contains two translationally nonequivalent and noncoplanar monomer units.²⁸ Yet, the spectroscopic properties are somewhat intermediate between those of planar blue chains and those of well-studied “standard” red PDAs such as poly-3BCMU isolated chains in their monomer crystal matrix,¹⁷ or poly-TCDU chains.⁷⁴ In particular, the Raman frequencies of poly-THD are intermediate between “red” and “blue” PDA values.⁷⁵

6.1. Structural and Energetic Properties. Three energetically close polymorphs (see Figure 10) were obtained from the experimental poly-THD structure²⁸ by torsion of the lateral substituents followed by geometry optimization leading to the closest local minimum. These three structures are certainly not the only possible ones, but we expect them to reproduce correctly the property changes. These three polymorphs are each characterized by their torsion angle and are named from it: 176-THD, 166-THD, and 114-THD. 166-THD was found by optimizing the experimental structure. The 176-THD structure was obtained from a starting guess with a 180° torsion angle between substituents, followed by optimization of the structure to the closest local minimum. 114-THD was obtained similarly from a starting guess at 125° . All of the structures show larger lattice parameters (by 3–8%) than the experimental one²⁸ (see Table 1). Such a discrepancy is within the range expected for GGA-DFT calculations of compounds with van der Waals interactions. 166-THD is similar to the experimental structure obtained from X-ray diffraction²⁸ with a comparable torsion in the carbon chain. A maximum deviation in the lattice constants below 5% and in the lattice angles below 2% suggests a correct

packing of the polymer chains with slightly too large interpolymer distances. All carbon–carbon bonds are reproduced within 2.2%.

176-THD is the least stable conformer (by $18\text{ kJ}\cdot\text{mol}^{-1}$ per monomer unit). 114-THD and 166-THD are nearly isoenergetic (see Table 1) as 114-THD is only $7\text{ kJ}\cdot\text{mol}^{-1}$ per monomer unit more stable than 166-THD. The maximum computed polymerization enthalpy for an optimized monomer is $135\text{ kJ}\cdot\text{mol}^{-1}$ per monomer unit at 0 K, in agreement with experimental results.⁷⁶

These torsion isomers can exist within a small energy range. The most twisted 114-THD isomer can even be the most stable one as expected from our previous model study.

6.2. Electronic Structure and Absorption Spectra. The band structures of the 166-THD and 114-THD isomers are presented in Figure 11 (the 176-THD structure is qualitatively close to that of 166-THD). The bands of the π -systems of these three conformers are similar to the ones previously studied for the model PDA except that flat bands associated with the diphenylamino substituents are also present. The highest occupied band is associated with the nitrogen lone pair that inserts into the gap between the π - and π^* -systems as shown in the projected density in panels 1 and 3 in Figure 11. The associated structure gaps are reduced in comparison with the same torsion in the model: the gaps are 530, 610, and 1520 meV for 176-THD, 166-THD, and 114-THD, respectively, whereas the model structure with the same torsion angles shows gaps of 860, 950, and 2400 meV, respectively. But the chain π – π^* gaps of the poly-THD conformers are quite similar to the model, namely 720, 750, and 2300 meV. The π -systems are thus weakly dependent on the nature of the substituents but are highly sensitive to torsion in the polymer backbone. The computed gaps cannot be compared directly with the experimental one (2.72 eV ³⁷ for diluted poly-THD in its monomer) as gaps calculated within DFT tend to be largely underestimated. Nevertheless, forms with so different band gaps and π – π^* transitions are expected to exhibit different colors.

The computed band-to-band absorption spectra of these three poly-THD conformers are presented in Figure 12. 114-THD absorbs in the blue part (400–500 nm) of the spectrum whereas 176-THD absorbs in the red part (600–800 nm). As for the model PDA (see section 5.1)), the relative positions of the absorption maxima deduced from these electronic structures indicate that 176-THD should be a blue PDA and 114-THD a red one. 166-THD is intermediate, with an absorption spectrum close to that of a red PDA, as experimentally observed.³⁷ Clearly, the variation of the torsion angle can be associated with a color change of the polymer.

6.3. NMR. The ^{13}C NMR chemical shifts were computed for these conformational isomers. The NMR spectrum of 166-THD, obtained with carbon and nitrogen atoms in the experimental geometry and all C–H bonds reoptimized, is shown in Figure 13 along with its assignment. The experimental features^{63,73} are well reproduced with an upfield CH_2 doublet, an aromatic region covering the 110–150 ppm range, and aromatic carbons bonded to nitrogen atoms in the 140–150 ppm area. The $\text{C}\equiv$ and $\text{C}=\text{}$ signals are shifted by about 10 ppm in comparison with the experimental spectrum (for poly-THD, the $\text{C}=\text{}$ experimental signal is hidden underneath the aromatic peaks, but it is typically observed around 130 ppm in PDAs).^{5,77} This variation could be due to a slightly incorrect optimized structure, as NMR

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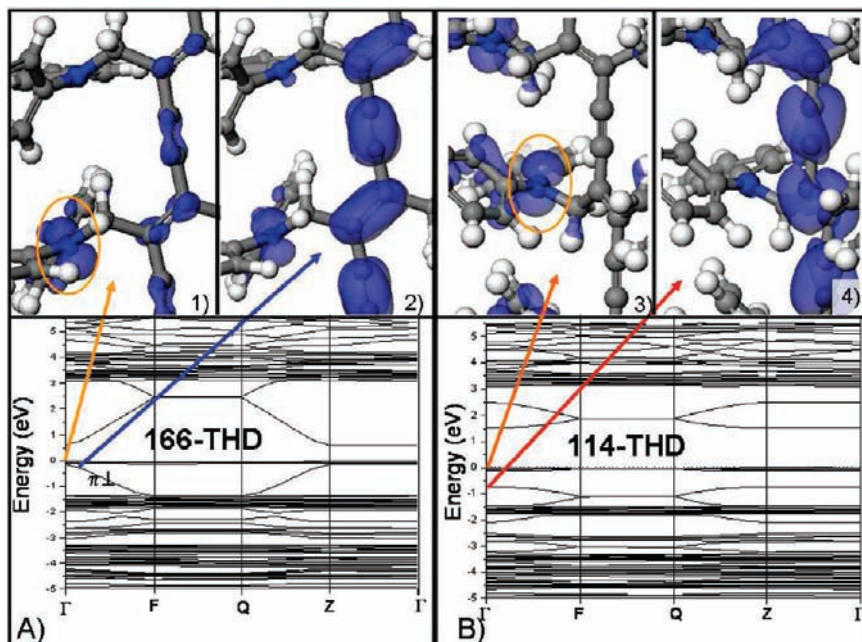


Figure 11. (A) Band structure of 166-THD using the same k -points as in Figure 5. π_{\perp} indicates the bands associated with the perpendicular π -system. (1) Projected electron density at Γ -point of the highest filled band (corresponding to the nitrogen lone pair) for 166-THD. (2) Projected density at Γ -point of the fifth-highest filled band (π_{\perp}) for 166-THD. (B) Band structure of 114-THD. (3) Projected electron density at Γ -point of the highest filled band for 114-THD. (4) Projected density at Γ -point of the fifth-highest filled band for 114-THD.

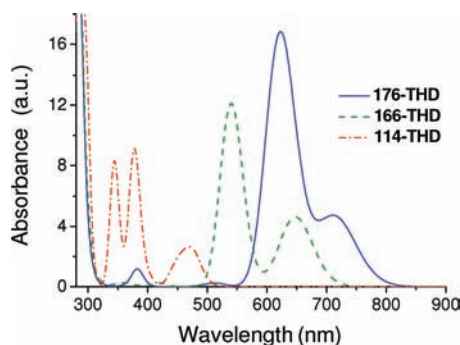


Figure 12. Calculated absorption spectra of various poly-THD polymorphs.

chemical shifts are strongly dependent on local environment, or due to the GGA-PBE functional that slightly overdelocalizes the electronic structure, amplifying artificially the aromatic character of the polymer chain. Nevertheless, the splittings of the nonequivalent CH_2 and $\text{C}\equiv\text{C}$ carbons are in very good agreement with those of the experiment: $\Delta\delta_{\text{CH}_2}$ (calculation) = 4 ppm vs 4 ppm (experimental); $\Delta\delta_{\text{C}\equiv\text{C}}$ (calculation) = 4 ppm vs 4 ppm (experimental). This splitting is weakly dependent on the size of the calculated cell and local geometry change; it seems to be dominated by chain torsion through a change in the positions of the aromatic rings, modifying drastically the local fields around the main chain.

The absolute values of the computed shifts are quite sensitive to unit cell volume. Since the latter is not constant for these conformers (see Table 2), we focus on the differences between the computed chemical shifts for nonequivalent $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ carbons and those observed experimentally.⁶³ These variations are given in Table 2. The nonequivalence nearly disappears for

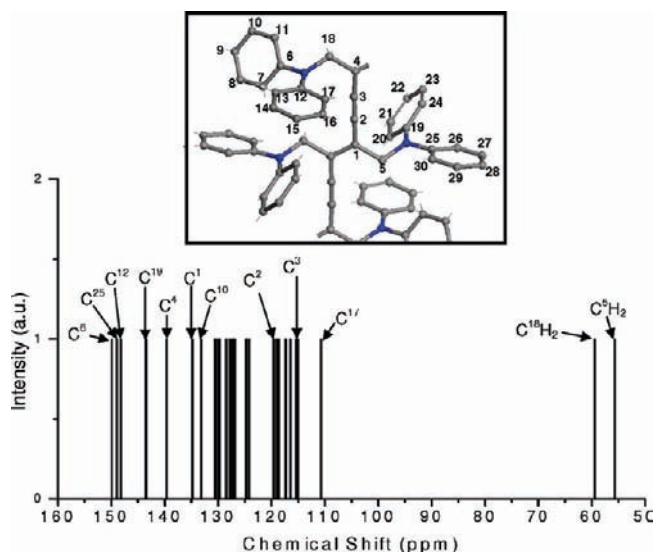


Figure 13. Calculated ^{13}C NMR spectrum of 166-THD optimized in the experimental unit cell. The most representative lines have been assigned.

114-THD, whereas it is maximum for 176-THD. The computed variation for the 166-THD structure is in agreement with the experimental one.⁶³

6.4. Vibrational Analysis. 6.4.1. Effect of Polymorphism on Vibrations. Finally, the vibrational frequencies of the symmetric $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$ stretches for all three poly-THD isomers are shown in Table 2. The vibrations associated with 114-THD are in very good agreement with a typical red phase PDA such as poly-TCDU ($\text{C}\equiv\text{C}$ stretch around 2110–2130 cm^{-1} and $\text{C}=\text{C}$ stretch at 1490–1530 cm^{-1});⁷⁸ also, the vibrations associated with 176-THD agree well with a typical blue phase PDA ($\text{C}\equiv\text{C}$

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Table 2. Comparison between the Properties of Computed and Experimental Poly-THD^a

	lattice parameters	C≡C(sym) (cm ⁻¹)	C=C(sym) (cm ⁻¹)	gap (eV)	color	Δδ ¹³ C C≡C (ppm)	Δδ ¹³ C C=C (ppm)
176-THD	$a = 9.81 \text{ \AA}$ $\alpha = 107.02^\circ$ $b = 9.87 \text{ \AA}$ $\beta = 109.71^\circ$ $c = 14.74 \text{ \AA}$ $\gamma = 86.97^\circ$	2062	1399–1414	0.534	blue	6	4
166-THD	$a = 9.34 \text{ \AA}$ $\alpha = 108.00^\circ$ $b = 9.85 \text{ \AA}$ $\beta = 105.70^\circ$ $c = 14.19 \text{ \AA}$ $\gamma = 88.08^\circ$	2058 (2088)	1310–1410 (1314–1418)	0.605 (0.597)	red	5 (4)	4 (5)
114-THD	$a = 9.64 \text{ \AA}$ $\alpha = 105.92^\circ$ $b = 9.83 \text{ \AA}$ $\beta = 99.62^\circ$ $c = 14.42 \text{ \AA}$ $\gamma = 84.74^\circ$	2121 (2078)	1492 (1452)	1.522 (1.091)	orange-red	1	0
Experiment ^{63,28,50,94}	$a = 9.05 \text{ \AA}$ $\alpha = 109.67^\circ$ $b = 9.74 \text{ \AA}$ $\beta = 109.08^\circ$ $c = 13.65 \text{ \AA}$ $\gamma = 85.51^\circ$	2105–2111	1480–1504	2.727	red	4	–

^a The data given in parentheses for 166-THD and 114-THD were computed for the structure optimized in the experimental unit cell. The variations of the chemical shift difference Δδ for nonequivalent carbons of the C≡C and C=C bonds are given.

stretch around 2060–2090 cm⁻¹ and C=C stretch around 1400–1460 cm⁻¹).⁷⁹

Frequencies were also computed for 166-THD. These frequencies are similar to the ones found for 176-THD, typical of a “blue” phase, despite the calculated “red” color. 166-THD frequencies are also at the lowest limit of the “red” phase range. This particular behavior of poly-THD might be rationalized by the mixing of the nitrogen lone pair with the π-system (see Figure 11A), giving further electronic conjugation and therefore decreasing further the frequencies.

6.4.2. Sensitivity to Stress and Unit Cell Size. Spectroscopic properties of PDAs are sensitive to hydrostatic pressure.^{2,41,75} Since the optimized unit cell is larger than the experimental one, this may affect the results. The effects of this difference were investigated by computing the vibrational frequencies and energy gap for the structure optimized in the experimental unit cell, starting from both 166-THD and 114-THD. The results are presented in Tables 1 and 2. The stressed structures show a nearly isotropic stress tensor: the stress can roughly be associated with a hydrostatic pressure.

First, the strained 114-THD structure resulting from a 12 kbar stress shows a large shift to lower frequencies (i.e., toward the “red” PDA range), associated with a strong decrease in the DFT gap. This can be traced to a reorganization of the structure and a large change in the torsion angle to 135°, in agreement with our model. In this case, we have an indication that the experimental barochromism can be linked to a change in the polymer torsion induced by the applied pressure.

The strained 166-THD structure under a 9 kbar stress shows an increase (30 cm⁻¹) of the C≡C vibration frequency, whereas the C=C vibration and the DFT gap are unchanged. The torsion angle is unchanged (165°). The C≡C frequency change can be traced to a slightly shortened C≡C bond (by 0.005 Å, see Table 1).

Stress on the unit cell seems to have two major effects on PDAs: a direct strain on the carbon–carbon bond lengths of the main polymer chain and an indirect strain on the torsion angles of the substituents. Depending on the polymorph type and applied stress tensor, the leading strain may be different. A more detailed study of the relationship between applied stress and polymer strain is underway.

6.5. Discussion. In this part, we have shown that the computed isomer 166-THD is close to the experimental structure, and we have computed two additional polymorphs, 176-THD and 114-

THD, which were found to be energetically very close or even more stable than 166-THD. Such a small energy difference is consistent with a possible phase change between structures induced by an external stimulus such as temperature, pressure, etc. This phenomenon is demonstrated in our calculated structures: under a 0 bar pressure (and 0 K), 114-THD is 7 kJ·mol⁻¹/monomer unit more stable than 166-THD, while at about 10 kbar, 166-THD becomes about 5 kJ·mol⁻¹/monomer unit more stable than 114-THD due to differences in their compressibilities. Clearly, the stability of these calculated polymorphs may be reversed by changing the external pressure.

The calculated absorption spectra of these polymorphs have maxima in the visible region at about 470 nm (114-THD), 540 nm (166-THD), and 630 nm (176-THD), that should roughly correspond, to the human eye, to an orange-red, a red, and a blue color, respectively. This is consistent with the experimental color of 166-THD. Furthermore, these colors would be the ones expected for a typical red/blue isomerism in PDAs.

Calculated NMR shifts are highly sensitive to local geometry, yet it may be concluded that the chemical shift splittings for nonequivalent carbons are strongly sensitive to the type of polymorph.

Finally, vibrational frequencies measured by Raman scattering have often been used in the literature to discriminate between “red” and “blue” phases. Specifically, two intense lines near 1500 and 2100 cm⁻¹ have been assigned to C=C stretch (ν_D) and C≡C stretch (ν_T) symmetric vibrations, respectively. While it is true that blue PDA have ν_D in the range 1440–1480 cm⁻¹ and many nonblue ones around 1520 cm⁻¹, this is not absolutely general (shifts due to strain^{41,42} are not considered here).

The fact of speaking of pure bond stretching vibrations is approximate. Our calculations yield full dynamical matrices and the atomic motions for each mode are determined, including the side groups. Unlike in the present study, calculations have been performed in the past^{78,80} on a simplified model of the chain containing 6 atoms, and in 2D. A complete analysis will not be given here; we only point out that atomic motions are in fact much more complex. For instance, for 166-THD in the experimental cell, the C=C symmetric stretch is spread over four main symmetric modes calculated at 1417 cm⁻¹ (which accounts for 24% of the total C=C symmetric stretch), 1408 cm⁻¹ (43%), 1340 cm⁻¹ (9%), and 1314 cm⁻¹ (12%) due to strong mixing with the symmetric CH₂ scissor motion. This may account for the presence of several lines between 1300 and 1500

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cm^{-1} in the preresonant Raman spectrum of poly-THD.⁵⁰ A similar explanation has been proposed by Bloor⁸¹ to account for the presence of several lines in the same frequency range in the Raman spectrum of poly-DCH.

To assign fully a resonance Raman spectrum, symmetry considerations (and the magnitude of the matrix elements) have to be taken into account. The symmetry of poly-THD is low, mainly due to the side groups; therefore, strictly speaking, normal modes cannot be classified as symmetric or antisymmetric as they can in our model PDA and in most PDA that have been studied. However, the conjugated chain itself almost retains a C_2 axis so that modes nearly antisymmetric to this operation should be weak in a Raman spectrum. The normal mode with the highest C=C stretch contents is, in fact, a mode at 1536 cm^{-1} (that accounts for 82% of the total C=C antisymmetric stretch), which is not inactive due to the loss of symmetry and might account for the relatively weak line observed at 1564 cm^{-1} ,⁵⁰ which is absent in most other PDAs.⁷⁸

The calculated main C=C symmetric stretching frequencies ($1408, 1417 \text{ cm}^{-1}$), that would be expected to be the intense ones, are then associated with the 1480 and 1492 cm^{-1} experimental lines. The associated error is larger than what would be expected for such calculations (typically on the order of $30\text{--}40 \text{ cm}^{-1}$), that can be linked to either a calculation problem caused by overconjugation of the polymer chain caused by DFT, by the small geometry difference between the calculated structure and the experimental one, or by a wrong attribution of the experimental/theoretical lines as the low symmetry makes it more difficult to assign correctly the Raman lines. Calculation of the Raman intensities would be needed to conclude, but it cannot be done realistically for such large systems with a reasonable computational cost. All the other lines of calculated 166-THD can be associated with the experimental ones within the typical error.

Nevertheless, the variations of the symmetric Raman frequencies and absorption spectra between 176-THD, 166-THD, and 114-THD are large enough to conclude that the polymorphism in the poly-THD structure associated with chain torsion has properties similar to the one of a red/blue PDA isomerism: 114-THD behaves like a typical “red” phase PDA while 176-THD behaves like a “blue” one. 166-THD is intermediate between the two, with a red color and a calculated Raman spectrum closer to that of a blue phase: 166-THD is intermediate, possibly being a “purple phase”.

In conclusion, we have shown that different PDA polymorphs associated with a torsion isomerism exist within a small energy range that is compatible with a possible phase transition between these polymorphs. Such a phase transition occurs in our calculations under an applied pressure. These polymorphs have spectral properties (optical and Raman spectra) compatible with a red/blue isomerism. Furthermore, the small changes in distance between main chain carbon atoms, that can be induced by an applied stress, do not have a strong enough impact to explain, alone, all property changes associated with a red/blue isomerism in PDAs. On the basis of our calculation results, a change in the twisting of the lateral groups has to take place to have a large impact on all spectral properties. Perhaps, other mechanisms, yet to be discovered and validated, could also explain this isomerism, but these calculations tend to confirm that the red/blue isomerism can be linked, at least in some cases, with lateral group twisting as previously proposed.

7. Discussion on Thermochromism

Chromoisomerism has been known to exist for a long time.⁸² An example of the complexity of such a system can be found in 5-methyl-2-[(2-nitrophenyl)amino]-3-thiophenecarbonitrile (ROY) that presents at least nine polymorphs associated with different colors going from yellow to red.⁸³ Nevertheless, the relationship between a crystal structure and a color is in most cases difficult to establish. Furthermore, things can become more complex when an external stimulus like temperature induces a phase change between these polymorphs. We shall focus in this section on how to explain the thermochromism found in PDAs. The present work deals with perfectly ordered chains and shows theoretically that they can have different colors. Such red chains are now experimentally known.^{8,17} This shows that disorder is not necessary to explain different colors and color transitions.³⁹

We have seen previously that the two torsion isomers of PDAs are good models for the blue and red phases. Many PDAs with different lateral substituents show similar colors, NMR, and Raman spectra. PDAs can be broken down into two subunits: the main polymer chain and the substituents. The polymer chain, depending on its torsion, gives the properties of the PDA: its color, Raman and NMR signature. The substituents, depending on their interactions with their surrounding, can induce some torsion of the main chain. PDAs show two kinds of thermochromism: an irreversible one and a less common reversible one.

7.1. Reversible Thermochromism. Reversible thermochromism was first observed in several crystalline PDAs in which the substituents contain urethane groups forming H-bond chains parallel to the polymer backbone.^{4,84–88} These crystals are always blue at lower temperature; on heating, there is a first-order phase transition to a red phase at a temperature between 105 and $140 \text{ }^\circ\text{C}$, depending on the PDA. An exception is TCDU which is red at $20 \text{ }^\circ\text{C}$ with a phase change at low temperature.⁷⁹ On cooling, the red to blue transition is observed between 75 and $105 \text{ }^\circ\text{C}$, and thus, a large hysteresis exists.⁸⁹ The transition generates some disorder.⁵ From room temperature to just below the transition temperature the unit cell volume increases by 2.5 to 5% .⁸⁷ This is comparable to what is found here between the experimental and theoretically optimized unit cells for 166-THD, with a difference in energy per monomer of $20 \text{ kJ}\cdot\text{mol}^{-1}$ (Table 1), but with equal θ angles and without major spectroscopic changes. At the transition, unit cells again increase by 2.5 to 3% , which is similar to the difference between 166-THD and 114-THD. We do not pretend, however, that our calculations provide a good model for the experimental transitions^{4,84–88} since THD lacks the H-bond ladders that these PDAs contain.

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However, other examples of reversible thermochromism can be found in PDA LB films and similar structures.⁹⁰ In some of these cases, there are indications that the red phase is in fact more ordered.⁹¹ Therefore, thermochromism is a more general phenomenon, not necessarily related to the presence of H-bonds, and in that framework, we believe that our results provide a useful computational analogy.

7.2. Irreversible Thermochromism. Free energies of the various possible phases may be too different to allow reversibility. A fairly common example is the blue-to-red transition during photopolymerization of LB films.¹⁸ Evidence also exists for such a transition during polymerization of some DA crystals, for instance, 3,5-octadiyne-1,8-diol.⁹² In that case, the monomer crystal structure only allows formation of blue chains by the known topotactic polymerization reaction; however, as the reaction proceeds, the increase in polymer contents induces a unit cell distortion and growing elastic stresses that finally lead to a red phase Raman spectrum.

In some cases, the blue polymer is formed up to complete reaction although the lowest free energy state of the chain is “red”: the energy barrier to the red phase is too high. However, if the polymer crystal is soluble or melts without decomposition, the solid polymer phase recovered on cooling or precipitation is red. An example is poly-4BCMU.⁹³ Examples of blue-to-red transition irreversibility are very common, while red-to-blue are very rare. Apparently, the lowest free energy state of a PDA is generally red.

7.3. Multistep Color Transitions. There is growing evidence that a third form can be observed between the blue and red ones, which has been coined the purple phase.^{5,20,21,43,44} A sequence of transitions blue-to-purple-to-red is then observed. In that case, three states are possible, as found for poly-THD in the present study.

Nothing excludes the possibility of having several phases of different colors in a given PDA and therefore the existence of multistep transitions. However, if an isosbestic point is observed (which is often the case), this is strong evidence of the absence of intermediates.

Experimentally, in poly-THD, none of the possible transitions is apparently observed, although a firm conclusion will require studies as a function of temperature (which are in progress) or pressure. Nevertheless, evidence for a surface phase of poly-THD can be found in the literature.⁹⁴

The geometry of poly-THD is the result of the complex interplay of many weak interactions in the crystal; it is likely that a similar calculation carried out on other systems would end up with slightly different geometries if nonplanar. As we point out, several species may result from the fact that the twist angle is not fixed irrespective of the overall crystal structure. We believe that the present study will contribute to clarification of the problem of color transitions in PDAs.

8. Conclusion

In this work, we have shown that isomers of nearly equal energies may exist in PDAs associated with a twist of the main chain substituents. The isomerization energy is low enough to be influenced by steric and entropic effects of the substituents. Phase transitions (in particular induced by pressure) can happen. This isomerism strongly modifies the electronic structure of the polymer chain and induces a shift of the absorption peaks from the red part of the spectrum for the planar structure to the blue region for the twisted structure. This is in good agreement with the observed reversible and irreversible chromism between “blue” and “red” forms. The experimental shifts in the Raman and NMR spectra between the “blue” and “red” isomers are also well reproduced by this isomerism.

Furthermore, three polymorphs of poly-THD have been found: a PDA crystal may indeed exist in more than two colors, with different chain geometries and optical properties. In one form the chain is planar within the uncertainties of the calculation; this corresponds to the absolute energy minimum of the chain but is the least stable isomer because of interactions between side groups. The second form is slightly twisted and the twist angle is equal to that in the known crystal structure; qualitatively, the absorption is significantly blue-shifted by comparison with the planar structure, despite the small twist angle, and most vibrational frequencies are close to the experimental ones. A third, much more strongly twisted polymorph, is slightly more stable than the previous one. Unfortunately, there is no experimental determination of the twist angle in known red PDAs other than THD, so one cannot conclude at this stage if this third structure is a typical red one. That it is not the actually formed structure is probably a consequence of the topochemical constraints on polymerization. Such a situation is indeed that of poly-4BCMU, where the as-polymerized crystal is blue, while the relaxed chain geometry is red. It should also be noted that poly-THD shows some evidence of electronic coupling of the N atoms with the polymer chain, as shown by the calculated electron densities (see Figure 11).

We have demonstrated that *ab initio* computation allows the study of complex polymers and the investigation of the relationship between their structures and their properties. Modeling can be used as a tool to design new PDA systems with specific properties.

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Supporting Information Available: All crystallographic data for the optimized geometries in the CIF format and absolute energies, calculated NMR chemical shifts and assignments for all of the carbons for experimental poly-THD. For 166-THD in the experimental cell, computed vibrations (at a 700 eV energy cutoff) that have a contribution on the main chain C=C stretch. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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