tions have different reactivities not only in termination but also in propagation because the trapped radicals in fact are not readily accessible to monomers. The probability of a radical center becoming trapped is a strong function of its chain length, and therefore, chain length dependent propagation as well as termination may be relevant. Any attempt at modeling such a polymerization process must properly account for these radical trapping effects.

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Theoretical Investigation of Gas-Phase Torsion Potentials along Conjugated Polymer Backbones: Polyacetylene, Polydiacetylene, and Polythiophene

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ABSTRACT: We present ab initio quantum-chemical calculations on the gas-phase torsion potentials of oligomers representative of polyacetylene, polydiacetylene, and polythiophene. Our goal is to obtain reliable values for the total energies involved in the torsions of fully conjugated chains, in order to assess the flexibility of such chains in solution and to provide the basis for meaningful discussions of persistence length and conjugation length models. Rotation around a single bond leads to barrier heights on the order of a few kilocalories per mole in polyacetylene and polythiophene (about 6 and 3 kcal/mol, respectively) but lower than 1 kcal/mol in polydiacetylene.

I. Introduction

One of the major advances in the field of conducting polymers has been the recent advent of conducting polymer solutions. Solutions of poly(*p*-phenylene sulfide) were first obtained by Frommer and co-workers; however, the solvents were rather exotic, such as an arsenic trifluoride–arsenic pentafluoride mixture.[1,2] More recently, Elsenbaumer et al.,[3] Sato et al.,[4] and Hotta et al.[5] turned their interest to polythiophene and found that the addition of long flexible alkyl chains (containing four or more carbons) on position 3 of the thiophene rings allows the polymer chains to become soluble in common organic solvents such as chloroform, dichloromethane, or tetrahydrofuran. The addition of an ethane- or butanesulfonate group, as considered by Wudl et al. or Meijer et al.,[6] renders the polymer chains soluble in water and leads to the concept of self-doped polymers when the chains are oxidized.

Intrinsic solubility (i.e., without side-chain addition) has been discovered for polyaniline. This polymer is soluble in concentrated sulfuric acid[7] and partially (or in some cases completely) soluble in organic solvents.[8]

These discoveries open the way to more complete characterization of conducting polymers as macromolecules

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(e.g., determination of the molecular weight). Furthermore, the dramatic improvements in the processibility of conducting polymers[9] pave the way toward the commercialization of stable, intrinsically conducting polymers.

The availability of conducting polymer solutions has not only boosted the application potentials of this class of compounds but has also opened up new areas of fundamental research in the field, such as (i) the investigation of thermochromic and solvatochromic effects and their dependence upon alkyl chain length[10-12] and (ii) spectroscopic studies aimed at understanding the possible differences between charge storage in a conducting polymer in solution and in the solid state.[13,14] In this framework, the studies performed on alkyl-substituted polythiophenes expand on the works devoted since the end of the 1970s to polydiacetylene, another conjugated polymer that is soluble in organic solvents.[15-17] Polydiacetylenes are not dopable to any significant level of electrical conductivity but present interesting thermochromic effects exploited in time-temperature indicators.[18]

In the solid state, it is well established that in the absence of strong steric interactions, crystal packing and the electronic energy associated with π-electron conjugation favor the appearance of coplanar conformations. In solution, the conformation is determined by the competition between the increased entropy of a disordered chain and the lower electronic energy of a fully conjugated coplanar chain. Thus, the very flexibility added to ensure solubilization can lead to significant deviations from planarity. Such deviations result in a lesser degree of conjugation and therefore directly influence those properties that are dominated by the π-electron framework. For instance, the solvatochromic and thermochromic effects in polyalkylthiophenes can be explained in terms of the appearance of torsions between adjacent thiophene rings, induced by the melting (or disordering) of the alkyl side chains.[19] In previous studies, we have examined the influence of the presence of a torsion angle on the electronic properties (such as bandgap, bandwidth, or ionization potential) of aromatic polymers.[20] These properties have been found to follow a simple cosine law as a function of the values of the torsion angle between rings.[20]

Here we are interested in going further by gaining some information about the torsion potential curves associated with conjugated macromolecules. Knowledge of the energies involved in the torsion process is essential if a meaningful discussion of the persistence lengths and conjugation lengths in solution is to be addressed.[21] We have chosen to examine oligomers representative of polyacetylene, polydiacetylene, and polythiophene. Up to now, polyacetylene has not been obtained in solution except in the form of block copolymers,[22,23] despite being the most studied conducting polymer. Nevertheless, recent advances in synthetic pathways, e.g., the ring-opening metathesis polymerization,[24,25] provide polymer chemists with improved tools to achieve solubilization of side-group-substituted polyacetylenes.

Our approach is to perform ab initio calculations either at the Hartree–Fock level or beyond Hartree–Fock by including correlation effects. Oligomers containing between 6 and 12 carbon atoms are considered and geometries as well as total energies are optimized as a function of torsion angle along the chains. Our methodology is presented in section II. Results are given in section III and discussed for oligomers of polyacetylene, polydiacetylene, and polythiophene. Conclusions of this work are presented in section IV.

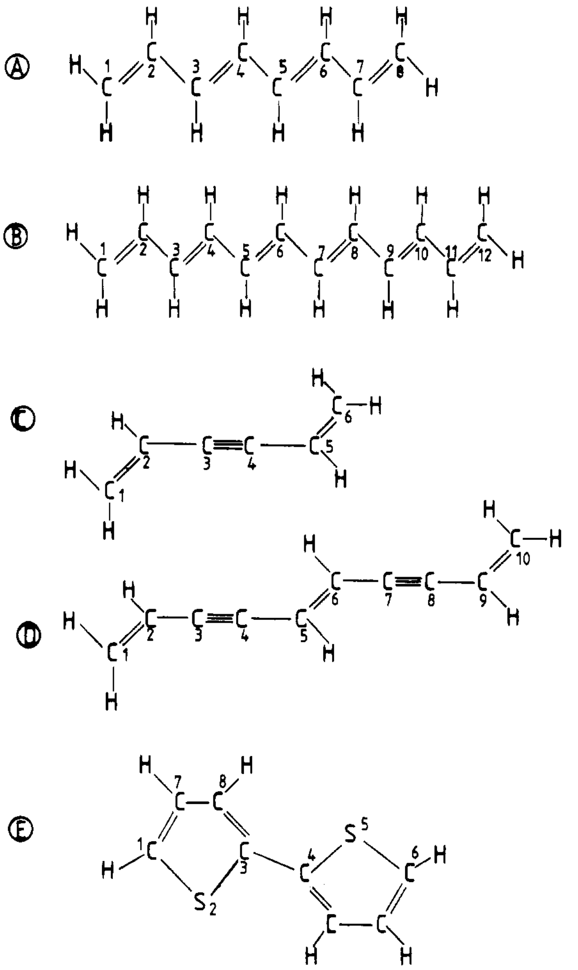

Figure 1. Sketch of the various oligomers investigated in this work: (A) octa-1,3,5,7-tetraene; (B) dodeca-1,3,5,7,9,11-hexaene; (C) hexa-1,5-dien-3-yne; (D) deca-1,5,9-triene-3,7-diyne; (E) bi-2,2′-thiophene.

II. Methodology

All the calculations reported in this work have been carried out with the Gaussian-86 set of programs,[26] as implemented on the Convex of the UCSB Materials Department. We have considered various oligomers containing between 6 and 12 carbon atoms; this makes it feasible to perform full geometry optimizations at a high basis set level: (i) for polyacetylene, octa-1,3,5,7-tetraene and dodeca-1,3,5,7,9,11-hexaene; (ii) for polydiacetylene, hexa-1,5-dien-3-yne and deca-1,5,9-triene-3,7-diyne; and (iii) for polythiophene, bi-2,2′-thiophene; see Figure 1.

Geometry optimizations are performed on the individual molecules at the restricted Hartree–Fock (RHF) ab initio level with a split-valence 3-21G basis set (a single basis function simulated by 3 Gaussians is used for the core atomic orbitals and two basis functions, simulated by 2 Gaussians and 1 Gaussian, are used for the valence atomic orbitals).[27] In the case of polyacetylene oligomers, we have fully optimized the geometry of octatetraene (all C—H and C—C bond lengths and all C=C—C and H—C—C angles) for (i) an all-trans coplanar conformation (torsions angles of 180° around all C—C bonds), (ii) a conformation for which there exists a 90° torsion around the central single bond, and (iii) a conformation that is of cis type (torsion angle of 0°) around the central single bond. Furthermore, single-point calculations, based on the geometry optimized for the all-trans conformation, have also been performed for situations where there occur torsion angles of 150°, 120°, or 90° around the central single bond or 90° around an external single bond. In the latter case, an ethylenic terminal segment becomes perpendicular to an hexatrienic segment; this situation appears experimentally to require the least torsion energy.[28] The geometry of dodecahexaene has been fully optimized in the all-trans coplanar conformation and kept frozen for a single-point calculation where there exists a 90° torsion angle around the central single bond.

Similar RHF/3-21G calculations have been carried out on the diacetylene oligomers. In those instances, torsions with respect to an all-trans coplanar conformation are performed around a single bond adjacent to the central triple bond. In the case of bithiophene (which represents the longest thiophene oligomer on which geometry optimizations with the 3-21G basis set are possible on our computer system), we have fully optimized the geometry for three values of the (S–C–C–S) torsion angle around the interring single bond: (i) 180° (anti conformation); (ii) 90° (perpendicular conformation); (iii) 0° (syn conformation). Additional single-point calculations based on the anti geometry have been carried out for torsion angles of 150°, 120°, and 90°.

We note that by performing calculations for 90° torsion angles, on the one hand allowing for full geometry optimization and on the other hand based on the 180° (coplanar) conformation geometry, we are in a position to determine the influence of the geometry relaxation on the barrier height.

We have also investigated the possible influence of electron correlation effects. To this end, we have carried out single-point calculations on the 3-21G relaxed geometries of the 180° and 90° conformations in octatetraene and hexadienyne, including correlation effects by performing the second-order Møller–Plesset (MP2) perturbation theory[29] and using a basis set containing d-polarization functions on the carbons (6-31G* basis set).[30] In the quantum-chemistry terminology, such an approach is usually denoted MP2/6-31G*//RHF/3-21G where "//" means "at the geometry of". The MP2 technique has been found in many instances to provide reliable trends in relation to the influence of correlation energy when going beyond the Hartree–Fock theory.[31]

Two features of our calculations need to be carefully borne in mind. First, the calculations are carried out on discrete molecules in the gas phase and not on polymers in solution. Therefore, for instance, all solvent effects are neglected. This can lead to some discrepancies with experimental data, especially when the torsion process generates a dipole moment, as in the case of bithiophene. Second, our calculations deal with torsions occurring along only one bond along the molecule. It is clear that actual polymer conformations involve multiple torsions all along the chains. The results of our calculations should, however, provide a reliable basis from which to address the problems of persistence/conjugation lengths in solution with statistical mechanics tools.[21]

III. Results and Discussion

A. Polyacetylene Oligomers. We first deal with the polyacetylene oligomers since precise estimates of the barrier for s-trans to s-cis isomerization have been reported by Ackerman and Kohler[28] on octatetraene. We are thus in a position to evaluate the reliability of our theoretical approach on such systems.

In Table I, we present the optimized geometries at the 3-21G level for octatetraene and dodecahexaene. For the coplanar conformations, we observe as expected that the degree of bond length alternation d (i.e., the difference between the length of a single bond and that of an adjacent double bond) slightly decreases as one proceeds toward the center of the molecule: $d = 0.139$ Å at the ends, $d = 0.129$ Å in the center of octatetraene, and $d = 0.125$ Å in the center of dodecahexaene. The very small evolution in bond lengths and bond angles in going from octatetraene to dodecahexaene indicates that only very small geometry variations are to be expected on further increase of the chain length. We note that the degree of bond alternation furnished by the 3-21G basis set is slightly larger than the X-ray scattering[32] and nutation NMR[33] experimental estimates, which are on the order of 0.08–0.10 Å.

Table I
Optimized RHF/3-21G Geometries of Octatetraene and Dodecahexaene as a Function of the Torsion Angle Value around the Central Single Bond[a]

Octatetraene

	180°	90°	0°
R(C1–C2)	1.322	1.321	1.322
R(C2–C3)	1.461	1.466	1.462
R(C3–C4)	1.328	1.322	1.328
R(C4–C5)	1.457	1.486	1.467
∠(C1–C2–C3)	124.1	124.0	124.1
∠(C2–C3–C4)	123.9	123.9	123.4
∠(C3–C4–C5)	124.1	123.6	127.0

Dodecahexaene

	180°
R(C1–C2)	1.322
R(C2–C3)	1.461
R(C3–C4)	1.329
R(C4–C5)	1.456
R(C5–C6)	1.330
R(C6–C7)	1.455
∠(C1–C2–C3)	124.1
∠(C2–C3–C4)	123.9
∠(C3–C4–C5)	124.1
∠(C4–C5–C6)	124.0
∠(C5–C6–C7)	124.1

[a] Bond lengths (*R*) are given in angstroms and bond angles (∠) in degrees. The atom labels refer to Figure 1.

In octatetraene, we have also optimized the geometries for the case where there is a 90° or a 0° torsion around the middle single bond. In the 90° situation, the torsion causes marked changes in the bond length values, especially that of the twisted single bond, which elongates by about 0.03 Å to reach 1.486 Å. The double bonds adjacent to it shorten by 0.006 Å to reach the same length as that of terminal double bonds in the 180° coplanar conformation. In the 0° angle case, the bond-length modifications are much smaller, the central bond elongating by some 0.01 Å with respect to the all-trans conformation. The major evolution is that of the C═C—C angles around the central bond, which increase to 127.0° from 124.1°. This opening allows the molecule to avoid any significant steric interactions between those hydrogen atoms that face one another.

The total energy results are presented in Table II. At the RHF/3-21G level, for a rotation around the central single bond and keeping the geometry frozen at its all-trans conformation value, we calculate the total energy to increase by 2.3 kcal/mol for a 150° angle and by 6.3 kcal/mol for a 120° angle, to reach a barrier of 6.9 kcal/mol for the 90° torsion. When relaxation of the geometry is allowed, the barrier is lowered, but merely by 0.4 kcal/mol to reach 6.5 kcal/mol. Using frozen geometries, we have also calculated the barrier that appears

Table II
RHF/3-21G and MP2/6-31G*//RHF/3-21G Total Energies of Octatetraene and Dodecahexaene as a Function of the Torsion Angle around the Central Single Bond[a]

	RHF/3-21G	MP2/6-31G*//RHF/3-21G
	Octatetraene	
180°	0.00	0.00
150°*	2.27	
120°*	6.13	
90°	6.47	5.53
90°*	6.88	
90°*[b]	6.34	
0°	3.35	
0°*	4.33	
	Dodecahexaene	
180°	0.00	
90°*	7.34	

[a] All energies are expressed in kcal/mol, relative to the energy of the all-trans conformation. Asterisks refer to cases where the geometry has been frozen at the bond length and bond angle values from the all-trans conformation. [b] Case where the torsion has been performed around an external single bond.

Table III
RHF/3-21G Upper Occupied One Electron Energy Levels of Octatetraene and Dodecahexaene as a Function of Torsion Angle around the Central Single Bond[a]

Octatetraene

180°	90°	90°[b]	0°
-7.60 (π)	-8.74	-7.95	-7.62 (π)
-9.94 (π)	-8.76	-10.12	-9.91 (π)
-11.89 (π)	-12.09	-10.76	-11.88 (π)
-13.13	-12.12	-12.78	-13.09 (π)
-13.14 (π)	-12.87	-13.01	-13.19

Dodecahexaene

180°	90°
-7.07 (π)	-7.96
-8.75 (π)	-7.97
-10.40 (π)	-10.77
-11.75 (π)	-10.79
-12.76 (π)	-12.80
-13.12	-12.80
-13.37	-13.00
-13.39 (π)	-13.35

[a] Energies are given in electronvolts. [b] Case where the torsion is performed around an outer single bond.

when the rotation takes place around an external single bond. The reason for this calculation is that, as mentioned before, there is experimental evidence that such a rotation is the lowest in energy.[28] We indeed find a barrier that is 0.6 kcal/mol smaller, i.e., 6.3 kcal/mol. Assuming that allowing for geometry relaxation would further lower the barrier by some 0.4 kcal/mol (as in the previous case), we obtain a theoretical estimate of about 5.9 kcal/mol. This result is in excellent agreement with the experimental measurements, which locate the barrier at 6.04 kcal/mol.[28]

We observe that the result of including correlation effects and using polarization functions is as expected to decrease the barrier height. The reduction we calculate is slightly less than 1 kcal/mol, thus not affecting the barrier qualitatively and keeping it at the same order of magnitude.

At the RHF/3-21G level, the cis conformation in its optimal geometry is calculated to be 3.4 kcal/mol less stable than the all-trans conformation for a rotation around the central bond. If we suppose that rotating around an external single bond would cost, as for the 90° case, around 0.6 kcal/mol less, we obtain a stability difference on the order of 2.8 kcal/mol, to be compared with an experimental value of 2.9 kcal/mol.[28] We note that in the case of the cis conformation, relaxation of the geometry exerts a larger influence on the total energy of the compound (lowering by about 0.9 kcal/mol, from 4.3 down to 3.4 kcal/mol) in order to avoid steric interactions as mentioned previously.

The total energy results obtained on octatetraene confirm that the RHF/3-21G methodology is capable of reliably predicting the trends in relative stabilities for different conformations of conjugated oligomers, which is the main goal of this work.

It is interesting to pay some attention to the one-electron energy levels, which are presented in Table III. We observe that twisting the octatetraene molecule around the central bond (which, from the π-electron standpoint, results in the formation of two butadiene subunits) leads to the near degeneracy of the upper two occupied π-levels, at -8.74 and -8.76 eV. These values are exactly midway between those for the upper two occupied π-levels in all-trans octatetraene, -9.94 and -7.60 eV. The near degenerate levels in 90° twisted octatetraene correspond to having the π-systems of each of the separate butadienic subunits interacting with the σ-levels of the other subunit. When the torsion is performed around an outer single bond, the upper π-level remains closer to the value it has in the coplanar conformation (-7.95 eV as compared to -7.60 eV) since it now originates from an hexatrienic subunit.

We also observe that the π-levels are almost identical in the coplanar (0 and 180°) conformations. This confirms that the π-levels are almost unaffected by the conformation as long as the chain remains coplanar. Such a result was also observed in polyacetylene itself for which the π-band characteristics are very similar when considering the all-trans, cis-transoid, and trans-cisoid conformations.[34]

In dodecahexaene, we have optimized the geometry for the all-trans conformation and kept that geometry frozen to calculate an "unrelaxed" barrier height. When twisting by 90° around the central single bond (which cuts the π-network into two hexatriene units), the barrier is calculated to be 7.3 kcal/mol, which is on the same order as but larger by 0.5 kcal/mol than that in octatetraene. As a result we expect that as the chain grows longer, it becomes more and more favorable to perform rotations around outer rather than inner single bonds. This behavior is consistent with the fact that when a conjugated chain is interrupted by an sp^3 defect, it is energetically more favorable to locate the defect toward a chain end.[35]

In 90° twisted dodecahexaene, the highest two occupied levels are almost degenerate (-7.96 and -7.97 eV). These values are similar to that of the HOMO level in end-twisted octatetraene since in both cases they originate in π-hexatrienic-like subunits. The next four levels are also degenerate two by two and appear at energies similar to those of two levels of end-twisted octatetraene.

We note that our estimate for the torsional barrier in polyacetylene oligomers is about 1 order of magnitude lower than that obtained on the basis of Hückel-type calculations where a 90° rotation around a single bond was considered to fully decouple the two chain subunits.[36] Actually, a Mulliken population analysis of our ab initio wavefunctions indicates that the total (π plus σ) bond orders are essentially *unaffected* by the torsion, even that for the single bond around which the rotation is carried out. At the ab initio level, even though π-conjugation is broken, there remains a strong coupling between the two chain subunits (the π-framework of one subunit interact-

Table IV
Optimized RHF/3-21G Geometries of Hexadienyne and Decatrienediyne as a Function of the Torsion Angle Value around an Inner Single Bond[a]

Hexadienyne

	180°	90°	0°
R(C1–C2)	1.322	1.321	1.322
R(C2–C3)	1.429	1.431	1.429
R(C3–C4)	1.193	1.192	1.193
∠(C1–C2–C3)	123.6	123.6	123.6

Decatrienediyne

	180°
R(C1–C2)	1.322
R(C2–C3)	1.428
R(C3–C4)	1.193
R(C4–C5)	1.424
R(C5–C6)	1.329
∠(C1–C2–C3)	123.6
∠(C4–C5–C6)	123.5

[a] Bond lengths (R) are given in angstroms and bond angles (∠) in degrees. The atom labels refer to Figure 1.

Table V
RHF/3-21G and MP2/6-31G*//RHF/3-21G Total Energies of Hexadienyne and Decatrienediyne as a Function of the Torsion Angle around an Inner Single Bond[a]

	RHF/3-21G	MP2/6-31G*//RHF/3-21G
	Hexadienyne	
180°	0.00	0.00
150°*	0.14	
135°*	0.27	
120°*	0.41	
90°	0.54	0.51
90°*	0.55	
0°	0.00	
	Decatrienediyne	
180°	0.00	
90°	0.71	

[a] All energies are expressed in kcal/mol, relative to the total energy of the 180° conformation. Asterisks refer to cases where the geometry has been frozen at the bond length and bond angle values of the 180° conformation.

ing with the σ-framework of the other subunit and vice versa), which stabilizes the *total* energy of the chain. Such a coupling is not taken into account at the simple Hückel level.

B. Polydiacetylene Oligomers. The optimized geometries obtained for the diacetylene oligomers are presented in Table IV. In the coplanar conformation of hexadienyne, the 3-21G optimized bond lengths (1.193, 1.322, and 1.429 Å for the triple, double, and single bonds, respectively) compare very well with those optimized for the polymer by Karpfen,[37] using a similar basis set (1.194, 1.321, and 1.425 Å), as well as those experimentally determined, e.g., for the p-toluenesulfonate (PTS) polymeric derivative (1.191, 1.356, and 1.428 Å[38]). We note that the experimental double bond is observed to be about 0.03 Å longer than the calculated value.

For hexadienyne, no significant difference in the geometry is found when a torsion angle of 90° or 0° is imposed around one of the single bonds. With respect to the all-trans conformation, the bond lengths are modified by at most 0.002 Å in the perpendicular conformation and remain identical in the cis conformation. We note, however, that, in the latter case, steric interactions would be present if bulky side groups, of the kind in p-toluenesulfonate, were explicitly taken into account. In the 90° conformation, the bond that evolves most is, as expected, that around which the torsion occurs. This lack of significant geometry evolution as a function of torsion results in very small total energy differences between relaxed and unrelaxed geometries at 90°. Increasing the size of the oligomer up to decatrienediyne also leads to negligible geometry evolutions. The inner double (single) bonds slightly elongate (shorten) by 0.007 Å (0.005 Å), the C=C—C angles remaining almost identical.

The total energy evolution as a function of torsion angle is presented in Table V. The most striking result is the very small height of the barrier calculated to perform a 90° rotation around a single bond. For hexadienyne, this barrier is found to be around 0.5 kcal/mol, with slight deviations depending on the level of calculation. At the 3-21G Hartree–Fock level, the barrier is 0.55 kcal/mol if the geometry is kept identical with that optimized for the 180° situation. The barrier is modified by an insignificant amount (lower by 0.01 kcal/mol) when the geometry is allowed to relax, consistent with the very small geometry evolution mentioned above. Increase of the basis set size to include polarization functions (6-31G*) and inclusion of correlation effects through the Møller–Plesset second-order perturbation theory sets the barrier value at 0.51 kcal/mol. In decatrienediyne, the unrelaxed barrier rises only slightly to 0.71 kcal/mol at the RHF/3-21G level.

That the barrier in polydiacetylene oligomers is 1 order of magnitude lower than in corresponding polyacetylene oligomers can be rationalized in the following way. As rotation around a single bond occurs, the double bond on one side of that single bond remains in conjugation with the triple bond on the other side. The feature originates from the two perpendicular π-systems carried by the triple bond. In that way, conjugation persists through the twisted single bond. The evolution of the one-electron energy levels is consistent with this picture. In the case of total rupture of conjugation, the HOMO level for 90° twisted decatrienediyne should appear at the same energy as that of the HOMO level for coplanar hexadienyne, i.e., at −8.42 eV. In fact, it is slightly less stable and is located at −8.24 eV, due to conjugation with the triple bond. As mentioned before, such an evolution is not present in the polyacetylene oligomers, where we have documented a total rupture of conjugation upon 90° rotation.

Such a small value of the barrier implies that a polydiacetylene chain can easily rotate around single bonds in good solvents, in particular in the absence of bulky side groups. Such groups, however, are almost always present and can hinder the rotation not only because of strong steric interactions (absent in our chain) but also due to the presence of hydrogen bonding through the lateral groups as in the 3-BCMU or 4-BCMU urethane-like side groups.

As pointed out by Rossi et al.,[21] it should be stressed that whenever the rotation around the single bonds is easy, it strongly affects the conjugation length. However, the persistence length is much less influenced; indeed, any rotation occurring around the virtual bond C2· · ·C5 has only a modest effect on the end-to-end distance, since the trans conformation of the double bonds imposes parallelism among all virtual bonds.

C. Polythiophene Oligomers. Due to the size of the monomer units, we have been restricted to optimization of the geometry only in the case of bithiophene. Some experimental data on the conformational preference of bithiophene have been reported by Bucci et al.[39] These authors have investigated bithiophene as partially oriented in the nematic phase of a liquid-crystalline sol-

Table VI
Optimized RHF/3-21G Geometry of Bithiophene as a Function of the Torsion Angle around the Inter-Ring Bond[a]

	180°	90°	0°
R(C1–S2)	1.794	1.794	1.791
R(S2–C3)	1.811	1.812	1.808
R(C3–C4)	1.441	1.447	1.445
R(C1–C7)	1.335	1.335	1.336
R(C7–C8)	1.444	1.447	1.443
R(C8–C3)	1.341	1.337	1.343
∠(C1–S2–C3)	89.5	89.4	89.7
∠(S2–C3–C4)	120.5	120.8	121.5
∠(S2–C1–C7)	111.8	111.9	111.7
∠(S2–C3–C8)	110.5	110.6	110.4

[a] Bond lengths (R) are given in angstroms and bond angles (∠) indegrees. The atom labels refer to Figure 1.

Table VII
RHF/3-21G Total Energies of Bithiophene as a Function of the Torsion Angle around the Two Thiophene Rings[a]

180°	0.00
150°*	0.34
120°*	1.74
90°	2.59
90°*	2.70
0°	1.96

[a] All energies are expressed in kcal/mol, relative to the total energy of the (180°) anti conformation. Asterisks refer to cases where the geometry has been frozen at the bond length and bond angle values of the anti conformation.

vent. NMR measurements indicate the anti conformation to be the most stable, with a barrier for conversion to the syn form of about 5 ± 2 kcal/mol.[39] A qualitative analysis of the data suggests that the stability difference between the anti and syn forms is very small, on the order of 0.2 kcal/mol.

Ab initio minimal basis set calculations by Barone et al.[40] predict a barrier height of 3.3 kcal/mol and a anti–syn stability difference of 1.05 kcal/mol. The barrier is thus calculated there to be on the low side of the experimental estimate. Contrary to what has sometimes been experimentally proposed, no local minimum is found outside of the coplanar conformations.[40] At the same level of calculation, similar results have been found by Brédas et al., with a barrier of 4.2 kcal/mol and a stability difference of 1.3 kcal/mol.[20]

In Table VI, we collect the 3-21G relaxed geometries for the anti, perpendicular, and syn conformations. As is usually obtained with the 3-21G basis set, the carbon–sulfur bonds are calculated to be somewhat too long with respect to the bond lengths measured via electron diffraction or microwave spectroscopy (calculated lengths of about 1.81 Å to be compared with experimental estimates of 1.72 Å). As rotation occurs around the central bond, small evolutions of geometries are found. In the perpendicular conformation, the interring bond length elongates from 1.441 Å up to 1.447 Å. In the syn conformation, we note that the inter-ring bond length remains intermediate between the previous two values (1.445 Å) and the angle between this bond and the C–S bond increases to 121.5°, a value 1° larger than in the anti conformation.

The barrier we calculate at the perpendicular conformation is 2.6 kcal/mol (2.7 kcal/mol, unrelaxed value), i.e., smaller than at the STO-3G level but also at the low side of the experimental data of Bucci et al.[39] On the other hand, we calculate that the anti conformation is more stable than the syn conformation by 2 kcal/mol, i.e., a difference 1 order of magnitude larger than the 0.2 kcal/mol proposed experimentally. At this stage, it is difficult to discriminate between the theoretical and experimental data. From the theoretical standpoint, the full geometry optimizations that we have performed for all three conformations should provide a reliable framework. However, as we have mentioned previously, we calculate the C–S bonds to be almost 0.1 Å too long. This could lead to an enhancement of steric interactions in the syn conformation. Furthermore, as mentioned in section II, the solvent effects are neglected in our approach. Polar solvents could preferentially stabilize the bithiophene syn conformation (for which we calculate a dipole moment of 2.4 D) with respect to the anti conformation (which has no dipole). From the experimental standpoint, on the other hand, it is not an easy task to evaluate how the nematic liquid crystal can influence the measured conformation of the bithiophene molecule.

Rossi et al.[21] have theoretically investigated the influence of the shape of the torsion potential on the persistence and conjugation lengths of polythiophene chains in solution. The differences between the potentials derived on the one hand from the NMR data of Bucci et al.[39] and, on the other hand, from our calculations are large enough that precise experimental measurements of these lengths should enable one to ascertain the relative quality of the two approaches. For instance, the persistence length at room temperature is calculated to be on the order of 11 polymer repeat units in the former case and about 60 in the latter case.[21] To the best of our knowledge, no relevant experimental data are available on unsubstituted polythiophene yet.

Finally, we note that the rigidity of the polymer backbone and therefore the persistence length should dramatically increase when the polymer is doped. Indeed, the doping process results in strong geometry modifications inducing quinoidic structures and thus double-bond character of the interring bonds.[41] Such a dramatic evolution of the persistence length has been recently reported by Aimé et al. through small-angle neutron scattering experiments on poly(3-butylthiophene).[42] These authors have found an increase in statistical length from about 55 Å up to >850 Å upon doping. Doped poly(3-butylthiophene) solutions display properties that are most interesting because they are markedly different from those of conventional polyelectrolytes.[42] In that context, the applicability of models, such as the conformon model proposed by Pincus et al.,[43] should be actively investigated.

IV. Synopsis

We have discussed ab initio quantum-chemical calculations on the torsion potentials of three conjugated polymers of high current interest, polyacetylene, polydiacetylene, and polythiophene. Our results show that the barrier heights for rotation around a single bond are on the order of a few kilocalories per mole, indicating that such chains should be rather flexible in solution.

In particular, our estimates for polyacetylene oligomers are in excellent agreement with the available experimental data. The barriers we calculate there are about 6 kcal/mol. Such values are 1 order of magnitude lower than those obtained on the basis of Hückel-type calculations where a 90° rotation around a single bond was considered to fully decouple the chain subunits. Accordingly, an examination of the Mulliken population analysis leads to the conclusion that the total bond orders are almost unaffected by the torsion (though conjugation is broken), even for the single bond around which the torsion is performed. The reason is that there remains a strong coupling between the two chain subunits, the π-

framework of one subunit interacting with the σ-framework of the other subunit and vice versa. As a result, the total energy of the chain is stabilized.

Geometry relaxations upon rotation are not very large; in the case of a 90° rotation, the twisted single bond elongates by about 0.03 Å and the double bonds adjacent to it acquire lengths similar to those of terminal double bonds. Electron correlation is not found to affect the results in a significant way.

In polydiacetylene oligomers, the barrier is calculated to be very small, on the order of kT. Such a small value is rationalized on the basis of the persistence of conjugation through the adjacent triple bond. In polydiacetylenes with bulky side groups, the picture can, however, be different because of interactions between the side groups. In bithiophene, the barrier is estimated to be on the order of 3 kcal/mol, i.e., on the low side of the experimental estimate. Doping of polythiophene-soluble chains should lead to large increases in torsion potentials because of the interring bonds acquiring a double-bond character. Such an evolution has already been observed experimentally.

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Registry No. $H_2C{=}CH(CH{=}CH)_2CH{=}CH_2$, 1482-91-3; $H_2C{=}CH(CH{=}CH)_4CH{=}CH_2$, 2423-92-9; $H_2C{=}CHC{\equiv}C\text{-}CH{=}CH_2$, 821-08-9; $H_2C{=}CHC{\equiv}CCH{=}CHC{\equiv}CCH{=}CH_2$, 82437-39-6; bi-2,2′-thiophene, 492-97-7; polyacetylene, 25067-58-7; polythiophene, 25233-34-5.