Theoretical *ab initio* investigation of the dipole polarizabilities of oligothiophenes and polythiophene

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Ab initio coupled and uncoupled Hartree-Fock polarizabilities are computed for increasingly large oligothiophenes using the 3-21G, 6-31G**, 6-311G**, and the Sadlej medium-size polarized atomic basis sets. The comparison with experimental values highlights the large sensitivity of the measured polarizabilities with respect to working conditions. By extrapolating to the infinite chain limit the polarizability values of increasingly large oligomers, we compute the asymptotic polarizabilities per thiophene ring. The transversal, perpendicular, and longitudinal asymptotic coupled Hartree-Fock polarizabilities per thiophene ring are, using the 3-21G (6-31G**) atomic basis set, 49.7 (52.5), 15.2 (20.6), and 184.1 (190.0) a.u., respectively. Polythiophene is more polarizable than polydiacetylene, polyyne, and polysilane but less polarizable than polyacetylene which, in contrast to polythiophene, is much more difficult to process. Using a procedure which relates the polarizability and the topology of the one-particle states, the major contribution to the polarizability is attributed to π -symmetry crystalline orbitals located at the top of the valence bands, which look like an alternation of segments of the highest occupied crystalline orbitals of the all-trans and trans-cisoid polyacetylene. However, a sizeable σ contribution comes from σ -conjugated segments formed by the sulfur atoms and their two adjacent carbon atoms.

I. INTRODUCTION

The electrical conductivities and nonlinear optical responses of conjugated polymers have attracted enormous attention among theorists and experimentalists during recent years.^{1,2} The synthesis and characterization of candidate systems for application in nonlinear optics is a tedious. way to investigate the field of these fascinating compounds. An alternative and complementary way is to use quantum chemistry which may help to orientate the synthesis towards the most interesting systems. Indeed, the methods of quantum chemistry provide numerical estimates of the properties, help the understanding of the phenomena, and finally lead to the establishment of structure-property relationships.³ The investigation of systems presenting high nonlinear effects is often limited to computing their linear optical responses due to the complexity and high sensitivity of calculations of second hyperpolarizabilities (for instance, to geometrical parameters and to the method used depending upon the semiempirical or ab initio nature of the Hamiltonian, the effects of inclusion of electron correlation and the size of the atomic basis set). Indeed, there is a relationship between the polarizability α and the second hyperpolarizability γ : large α are often associated with even larger γ . The interest brought about by π -conjugated systems lies in the large increase of the longitudinal polarizabilities and second hyperpolarizabilities in increasingly large oligomers.⁴⁻⁹ This increase is characterized by a nonlinear evolution of the longitudinal optical properties in the smallest chains. This is followed by a saturation and finally, the evolution becomes linear for the largest chains. These very large linear and nonlinear responses may be attributed to a substantial electron delocalization along the polymer backbone. In the other directions (perpendicular and transversal), the evolution of the polarizability is only additive with the size of the oligomers.

In this work, we deal with finite and infinite polythiophene chains. These are components of very interesting π -conjugated systems because of their stability in air and their solubility in most organic solvents when substituting some of the hydrogens by functionalized alkyl or phenyl lateral groups.¹⁰ For instance, polythiophene can be chemically oxidized to yield high electrical conductivities reaching the metallic regime,¹¹ or, in the pristine state, exibit large third-order nonlinear optical responses.¹²⁻¹⁴ The objectives of this work are (i) to compare the electric dipole polarizabilities computed theoretically with experimental measurements, (ii) to compare polythiophene chains with the most commonly studied π -conjugated systems, polyacetylene chains, and other systems such as polydiacetylene, polyyne, and polysilane, and (iii) to assign the polarizability of polythiophene to particular one-electron states.

Our work is organized as follows. First, we summarize and comment upon the experimental works of Zhao *et al.*¹³ and Thienpont *et al.*¹⁴ concerning the measurements of the

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TABLE I. Average polarizabilities of oligothiophenes according to the experimental conditions and the number, N, of thiophene rings. The values are given in atomic units (1.0 a.u. of polarizability=1.6488 10⁻⁴¹ C² m² J⁻¹=0.14 818 Å³).

N	Solution THF $\lambda = 589 \text{ nm}$	Zhao <i>et al.</i> ^a Thin films $\lambda = 632.8 \text{ nm}$	Solution THF $\lambda = \infty$	Thienpont <i>et al.</i> ^t Films PMMA $\lambda = 632.8 \text{ nm}$
1	66.9	66.0	55.9	······································
2	168.7	1	124.2	÷ *
3	303.7	153.6	195.8	74.2
4	674.8	202.8	377.7	94.5
5	1282.2	254.8	652.1	175.5
6	3036.7	315.0	1418.0	• •
7				445.4
11				472.4

^aReference 13.

^bReference 14.

average polarizability of oligothiophenes. We then compare these experimental values with *ab initio* results obtained at the sum over states¹⁵ and coupled perturbed Hartree–Fock¹⁶ levels using atomic basis sets of different size. These results on increasingly large oligothiophenes make it possible to estimate an asymptotic value for the longitudinal polarizability per unit length and the average polarizability per unit volume of polythiophene which is then compared to the linear electric responses of other compounds, namely, infinite polyacetylene, polydiacetylene, polyyne, and polysilane chains. Finally, using a procedure we recently proposed,¹⁷ we analyze the polarizability of polythiophene in terms of the topology of the oneparticle states which make the largest contributions to the longitudinal polarizability.

It is important to note that we have computed the static electronic contribution to the polarizability at the Hartree–Fock level which represents quite substantial computations in the case of the largest basis sets. Nevertheless, we are aware of the corrections which may be brought by taking into account electron correlation, by including the vibrational contributions and by treating the frequency-dependent character of the polarizability.

II. SUMMARY OF THE EXPERIMENTAL RESULTS

In Table I, we reproduce the experimental average polarizabilities $[\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3]$ measured by the groups of Zhao¹³ and Thienpont.¹⁴ Their procedures consisted of the measurement of the refractive indices and then the evaluation of the polarizability. Zhao *et al.*¹³ dealt with oligothiophenes both in THF solution and in the form of thin films. For the solutions, the wavelength used was the sodium *D* line ($\lambda = 589$ nm, $E = \hbar\omega = 2.11$ eV) while for the films, they used the quasi-wave-guide technique at the wavelength of the He-Ne laser ($\lambda = 632.8$ nm, $E = \hbar\omega$ = 1.96 eV). In the work of Thienpont *et al.*,¹⁴ the thiophene chains possessed methyl or butyl lateral groups allowing the synthesis of larger chains than those synthesized by Zhao *et al.*¹³ The chains were dispersed in a polymethylmethacrylate (PMMA) matrix. As Zhao *et al.*,¹³ Table I, large variations in the measured polarizabilities appear according to the technique used. Due to resonant enhancement, the frequency dependence of the polarizability leads to an increase of the linear response when the wavelength used decreased. In addition to the effect of the source frequency, the variation of this effect with the size of the oligomers also needs to be highlighted. Indeed, the excitation energies decrease with the elongation of the chain^{13,14,18} and cause a further increase of the polarizability. By using a model two-level system consisting of the ground and the first excited states, we may relate the zero frequency with the frequency-dependent polarizabilities by applying the formula

$$\bar{\alpha}(0) = \bar{\alpha}(\omega) \frac{\Delta E^2 - \hbar^2 \omega^2}{\Delta E^2}, \qquad (1)$$

where ΔE is the excitation energy from the ground to the excited states, ω the frequency of the electromagnetic wave, and \hbar Planck's constant divided by 2π . Using the excitation energies measured by Zhao *et al.*¹³ obtained on the oligothiophene in THF solution, we have calculated the polarizabilities extrapolated to zero frequency. These results are also given in Table I. However, this model is oversimplified because it does not take into account other excited states and resonance phenomena.

The comparison between both results of Zhao *et al.*¹³ clearly indicates that the modification of the intermolecular interactions in the solid state leads to a substantial decrease of the average polarizability. Moreover, the interactions between the alkyl substituents and the polymer matrix may lead to a further decrease of the polarizability resulting from a departure from planarity of the system. Thienpont *et al.*¹⁴ mentioned the thermochromism and solvatochromism associated with this phenomenon.

In conjugated systems, it would be expected that the average polarizability per unit cell $[\bar{\alpha}(N) - \bar{\alpha}(N-1)]$ first increases with the size of the system and then saturates.^{5,6} The oligothiophenes synthesized by Zhao et al.¹³ exhibit such an increase of the average polarizability per unit cell in both cases, i.e., in solution in THF or in the form of thin films. However, while saturation is apparent for the films, for the oligothiophenes in solution the increase is very large and the onset of saturation is not apparent yet for the hexamer. Moreover, the results obtained by Thienpont et al.¹⁴ on alkyl substituted oligothiophenes dispersed in a PMMA matrix are totally inconsistent with the increase of $\bar{\alpha}(N) - \bar{\alpha}(N-1)$. Indeed, the saturation of the average polarizability obtained in this case corresponds to a decrease in the average polarizability per unit cell as the chain grows. This is contradictory with what one would expect and, probably, we may relate this to an increase of the departure from planarity of the chains with increasing chain length.

Hence, the extreme sensitivity of the measured polarizabilities of oligothiophene chains with respect to the nature and the physical state of the chains clearly indicates the difficulty of exploiting these values in the characterization of the linear response properties of polythiophene



FIG. 1. 3D representation and geometrical parameters of polythiophene chains in Å and degrees.

chains. In the next section, by using theoretical chemistry methods, we propose to clarify the situation.

III. CALCULATION OF THE POLARIZABILITIES OF OLIGOTHIOPHENES

A. Geometrical considerations

In order to preserve the π conjugation through the system, which is responsible for the striking properties of polythiophene, the planar anti conformation with $\alpha - \alpha'$ connected rings was chosen. In the anticonformation, the sulfur atoms in adjacent rings point in opposite directions. Our choice is coherent with crystal data structures reported for 2,2'-bithiophene, terthiophene, and methylsubstituted quaterthiophenes which demonstrate a planar arrangement of the rings in the anti conformation.¹⁹ However, it is known that the alkyl substituents, which on heating undergo a rearrangement, lead to a departure from the planarity of the polythiophene backbone.²⁰ MNDO²¹ optimized geometrical parameters of the anti planar structure²² are chosen and are given in Fig. 1 for the repeating unit or translational unit cell of the polymer. Such an optimization procedure is known to provide acceptable geometrical parameters at low computational cost. In addition, the bond length alternation, which strongly influences the polarizabilities,⁴ is more accurately reproduced²³ than with abinitio Hartree-Fock methods suffering from the lack of electron correlation and yielding too large bond length alternations or than other semiempirical methods such as AM1 providing too short bond length alternations.²⁴ The same geometrical parameters are used for each thiophene unit of each oligomer, neglecting therefore the end chain effects on the geometry which are known to decrease in importance as the chain length increases.

B. Description of *ab initio* Hartree–Fock methods to compute the polarizabilities

In our calculations, the electronic structures have been determined at the *ab initio* Hartree–Fock level. In this approach, the electronic states of our oligomers are Slater determinants constructed from doubly occupied molecular orbitals represented by linear combinations of atomic orbitals. The polarizability tensors have been computed at the sum over states (SOS)¹⁵ and coupled perturbed Hartree-Fock (CPHF)¹⁶ levels using split-valence 3-21G,²⁵ and the extended 6-31G**,²⁶ and 6-311G**²⁷ atomic basis sets. We also employed the Sadlej mediumsize polarized basis set,²⁸ specifically designed to provide accurate estimates of molecular dipole moments and electric dipole polarizabilities. All the calculations were done using the GAUSSIAN 90 program.²⁹ Both the SOS and CPHF methods work in the space of the atomic orbitals. In the SOS approach, which is based on standard timeindependent perturbation theory, the polarizability tensor is the second order term (multiplied by -2) in the perturbation expansion of the energy as a power series in the applied external electrical field. The expression for the different components of the polarizability are given in terms of the unperturbed wave functions and energies. Commonly, one uses a Hartree-Fock ground state together with its singly excited determinants for the excited states.^{3,15} Hence, a component of the polarizability tensor reads as

$$\alpha_{xy} = 4 \sum_{i}^{\text{occ}} \sum_{a}^{\text{unocc}} \frac{(\phi_i | x | \phi_a) (\phi_a | y | \phi_i)}{\epsilon_a - \epsilon_i}, \qquad (2)$$

where the ϕ_i and ϕ_a represent doubly occupied and unoccupied molecular orbitals, respectively, ϵ_i and ϵ_a their corresponding orbital energies. The CPHF¹⁶ procedure corresponds to an analytical differentiation of the fielddependent Hartree–Fock equation. In this procedure, the field-induced electron reorganizational effects are included in a way which is fully consistent in terms of adjustments in the average two-electron interactions. For this reason, it is described as a *coupled* Hartree–Fock procedure whereas the SOS approach is said to be *uncoupled*.³

C. Effects of the basis set and the method used on the polarizability calculations

The transversal (α_{xx}) , perpendicular (α_{yy}) , and longitudinal (α_{zz}) polarizabilities computed at the uncoupled and coupled Hartree–Fock levels are listed according to the length of the chain and the basis set used in Tables II and III, respectively. Only the 3–21G calculations have been performed on the largest oligomers due to the excessive computational cost associated with the Sadlej polarized and extended basis sets.

First, we compare the effects of the basis set used on the CPHF polarizability estimates of the first oligothiophenes. The CPHF results obtained on the thiophene monomer with the medium-polarized basis set of Sadlej $(\bar{\alpha}=63.1 \text{ a.u.})$ correspond fairly well to the experimental values measured by Zhao *et al.*¹³ [($\bar{\alpha}=66.9 \text{ a.u.}$ in solution in THF and 66.0 a.u. in form of thin films) and Le Fèvre *et al.*³⁰ ($\bar{\alpha}=60.6 \text{ a.u.}$). Therefore, the values obtained with the Sadlej basis set are used as references for comparison. The split-valence 3–21G atomic basis set is known to provide a good compromise between basis set size and quality of estimates for the transversal and longitudinal components of the polarizability tensor. Indeed, these calculated Champagne, Mosley, and André: Polarizabilities of thiophenes

TABLE II. SOS transversal (α_{xx}) , perpendicular (α_{yy}) , and longitudinal (α_{xx}) components of the polarizability tensor of increasingly large polythiophene chains (*N* is the number of thiophene rings) according to the basis set used. These values are expressed in atomic units.

	N	3–21G	6-31G**	6–311G**	Sadlej
	1	62.52	66.32	69.01	76.17
	2	125.96	133.09	138.12	150.50
	3	189.09	199.65	207.02	
α_{xx}	4	252.20	266.20		÷
	5	315.30	332.74	1. 	
	6	378.40	- · · - ·		
	7	441.50			
	1	15.99	27.04	30.49	47.49
	2	32.14	53.54	59.46	89.11
	3	48.29	79.99	88.61	
α_{yy}	4	64.43	106.45		
	· 5	80.58	132.90		
	6	96.72	-		1
	7	112.86			
	1	55.41	58.22	60.32	69.16
	2	129.24	133.90	137.75	154.38
	3	211.79	217.94	223.53	
α,,	4.	296.97	304.42		•
—	5	382.84	391.51	-	
	6	468.86			
	7	554.92			

TABLE III. CPHF transversal (α_{xx}) , perpendicular (α_{yy}) , and longitudinal (α_{xx}) components of the polarizability tensor of increasingly large polythiophene chains (N is the number of thiophene rings) according to the basis set used. These values are given in atomic units.

	N	3–21G	6–31G**	6–311G**	Sadlej
	1	61.16	65.62	68.95	76.01
	2	113.91	121.30	126.82	137.63
	3	163.85	174.14	181.82	
α_{xx}	4	213,97	227.10		
	5	263.68	279.65		
	6	313.44			
	7	363.09			
	1	16.84	24.18	27.11	44.56
	2	32.22	45.19	49.61	77.15
	3	47.44	65.93	71.96	. •
$\alpha_{\nu\nu}$	4	62.61	86.61		
	, 5 .	77.77	107.25		
	6	92.92			
	7	108.07	·	2.1	
	1	55.46	58.31	60.23	68.80
	2	151.50	157.75	161.99	180.53
	3	282.27	292.81	299.84	
α_{77}	4	434.58	450.00		1
	5	599.56	620.27		
	- 6	771.98			
	7	948.92			

values correspond to 80% of the results obtained with the Sadlej polarized basis set or to the experimental value³¹ for the monomer. In fact, in the longitudinal direction and, to a lesser extent in the transversal direction, the quality of the basis set is improved. Indeed, the deficiency in the atomic basis set on any atom in one ring is compensated for by the atomic orbitals on neighboring rings and adjacent atoms in the same ring. This is especially apparent if conjugation and thus electron delocalization exist along the chain. However, this is not the case of the perpendicular component, which is poorly estimated due to the lack of extent of the atomic basis set in this direction: Only $2p_{y}$ atomic orbitals on the carbon atoms and $2p_v$ and $3p_v$ atomic orbitals on the sulfur atoms play a role in the calculation of the perpendicular component of the polarizability tensor.

Starting from the 3-21G polarizability estimates, our results demonstrate also the small differences obtained by using the $6-31G^{**}$ and $6-311G^{**}$ atomic basis sets, in contrast to the considerable improvement brought by the Sadlej polarized basis set. On average, only 30% of the gap between the Sadlej results and the 3-21G estimates is recovered by adding polarization functions and going from a double to a triple zeta description of the valence atomic orbitals. Most of the improvement concerns the perpendicular direction which is poorly described with the 3-21G atomic basis set.

The comparison between the SOS and CPHF polarizability values shows the importance of the field-induced electron reorganizational effects. Their inclusion enhances the polarizability component along the polymeric backbone, i.e., along the direction of electron delocalization. In contrast, the transversal and perpendicular components of the polarizability are only slightly affected. Since the major component of the polarizability is the longitudinal, the coupled Hartree–Fock procedure is more suitable than the uncoupled Hartree–Fock procedure to provide quantitative estimates of the polarizability of conjugated systems.

D. Effect of the chain length

As expected, the evolution of the transversal and perpendicular polarizabilities is linear with the size of the chain. Indeed, whereas the α_{yy} per unit cell is constant, the α_{xx} values per unit cell present small oscillations as the size of the chain increases. This phenomenon, only visible at the CPHF level, is linked to the variation of the chain symmetry, which alternates between the C_{2h} symmetry for an even number of rings and the C_{2v} symmetry for an odd number of thiophene units. Therefore, the results on the oligomers already provide acceptable estimates of the asymptotic value of transversal and perpendicular polarizabilities per thiophene ring of polythiophene. By using the 3-21G (6-31G**) atomic basis set, these estimates of the transversal and perpendicular components are 63.1(66.6) and 16.1(26.5) a.u. and 49.7(52.5) and 15.2(20.6) a.u., for the SOS and CPHF procedures, respectively.

However, this is not the case for the longitudinal component of the polarizability because the electron delocalization enhances the polarizability. Our approach is to follow the evolution of the polarizability in increasingly large oligomers as a function of the chain length, and then, to extrapolate the polarizability to the infinite polymer limit.⁵⁻⁹ As we recently proposed, an alternative procedure



FIG. 2. Evolution of the longitudinal polarizabilities $[\alpha_{xx}(N) - \alpha_{xx}(N - 1)]$ per thiophene ring of increasingly large oligothiophenes computed at the SOS and CPHF levels by using the 3-21G and 6-31G** atomic basis sets. Results are given in atomic units. The SOS results are represented by circles whereas the CPHF results by triangles. These circles and triangles are filled for the 3-21G polarizability values whereas they are empty for the 6-31G** polarizability values.

would consist in the direct calculation of the asymptotic value by performing the calculation on the polymer system, i.e., taking advantage of its translational symmetry.^{17,32–33} The knowledge of the asymptotic value of the polarizability illustrates the potential of a polymer to be applied in linear and nonlinear optics. As shown in Fig. 2, the curves representing the 3–21G and 6–31G** longitudinal polarizability per thiophene ring are already starting to level off in the seven unit chain. Although for the coupled Hartree–Fock procedure, the saturation regime is not yet reached, extrapolation procedures may be applied to predict the asymptotic value. This value is obtained by extrapolating to the infinite length the following expression:

$$\alpha_{\tau\tau}(N) - \alpha_{\tau\tau}(N-1) = a - be^{-cN}$$
(3)

of which the parameters were obtained by fitting the theoretical results. The asymptotic value for N equal to infinity is thus equal to a. We have recently argued that³³ such procedure provides at least as good asymptotic values for the longitudinal polarizability per unit cell as the 1/Npower series expansions proposed by Hurst et al.⁵ and Kirtman.⁶ Using the 3-21G atomic basis set, the asymptotic longitudinal polarizability per unit cell is 86.1 and 184.1 a.u. at the SOS and CPHF levels, respectively. Therefore, the average values are 55.1 and 83.0 a.u. for the uncoupled and coupled Hartree-Fock procedures, respectively. Because of the too small number of points in the fitting procedure, no accurate extrapolation procedure may be applied directly to obtain the asymptotic 6-31G** longitudinal polarizability per unit cell. However, as shown in Fig. 2, the 6-31G** longitudinal polarizability per unit cell presents an evolution with N parallel to the 3-21G longitudinal polarizability per unit cell. As the ratio 3-21G/6-31G** has already converged for the pentamer, it can be used to scale up the 3-21G asymptotic longitudinal polarizability per unit cell and to obtain as 6-31G** polarizability values 87.3 and 190.0 a.u. for the uncoupled and cou-



FIG. 3. Evolution of the average $[\bar{\alpha}(N) - \bar{\alpha}(N-1)]$ polarizabilities per thiophene ring of increasingly large oligothiophenes obtained either theoretically at the SOS (\bullet) and CPHF (O) levels by using the 3-21G atomic basis set or experimentally by Zhao *et al.* (Ref. 13) from solution of oligothiophenes in THF (*) or from thin films (\Diamond). The polarizability values are given in atomic units.

pled Hartree–Fock procedures, respectively. The average values per thiophene ring become 60.1 and 87.7 a.u., respectively.

In Fig. 3, we compare the evolution with respect to the chain length of the computed average polarizabilities per unit cell with the experimental values obtained by Zhao *et al.*¹³ This figure illustrates the nice saturation behavior of the computed polarizabilities per unit cell with respect to the chain length in contrast to the substantial increase obtained on the oligothiophenes in solution in THF as the chain contains more than three thiophene units. The possible reasons of such a behaviour have been discussed in Sec. II.

E. Derivation of scaling factors

The underestimate in the polarizability (especially in the perpendicular direction) associated with the finite size of the 3-21G atomic basis set may be alleviated by using scaling factors between the 3-21G results and the Sadlej basis set values. This technique proposed by Chablo and Hinchliffe³⁴ has already been used by Bodart et al.³⁵ for unsaturated hydrocarbon chains. The scaling factors are extracted from $\alpha(2) - \alpha(1)$, the polarizability differences between bithiophene and thiophene obtained at the CPHF level. From the computational point of view, larger systems are out of reach because of the big size of the Sadlej polarized atomic basis set. However, the validity of our procedure is supported by the fact that the ratios between the polarizability differences, $\alpha(N) - \alpha(N-1)$, calculated by using the 3-21G and 6-31G** or 6-311G** atomic basis sets do not present anymore significant changes for Nlarger than 2. These scaling factors are 0.86, 0.47, and 0.86 for the x, y, and z components of the polarizability tensor, respectively. Therefore, we derive an improved estimate of the electric dipole polarizability tensor per unit ring: α_{yy} N=58.1 a.u., $\alpha_{yy}/N=32.2$ a.u., $\alpha_{zz}/N=214.1$ a.u., $\bar{\alpha}/N$ = 101.5 a.u. as \tilde{N} tends to infinity. The calculation of scaling factors between the 6-31G** and Sadlej basis set

TABLE IV. Comparison of the CPHF asymptotic longitudinal and average polarizabilities per unit cell, unit length and unit volume of polythiophene with all-*trans* and *trans-cisoïd* polyacetylene, polydiacetylene, polyyne, and polysilane. All values are given in atomic units except the bond length alternation, Δr , in Å.

	Δr	Atomic basis set	$\frac{\alpha_{zz}}{N}$	$\frac{\alpha_{zz}}{L}$	$\frac{\overline{\alpha}}{\overline{N}}$	$\frac{\overline{\alpha}}{V}$
Polythiophene	0.064, 0.067	3–21G	368.1	25.1	166.0	9.6
$-[C_8S_2H_4]_{\infty}-$	0.064, 0.067	6–31G**	380.0	25.9	175.4	10.1
,	0.112ª	6–31G	163.3	35.1	60.3	16.0
All-trans polyacetylene	0.112 ^a	6-31G*	154.8	33.2	57.0	15.1
-[C,H]	0.112 ^a	6-31G+PD	160.5	34.5	60.8	16.1
	0.082 ^b	3–21G	220.7	47.1	81.4	21.4
	0.123°	3–21G	151.6	32.6	57.9	15.3
Trans-cisoïd polyacetylene	0.082	3–21G	206.7	49.6	76.2	20.2
-[C ₂ H ₂] _∞ -	0.123	3-21G	124.3	28.9	48.3	12.8
Polydiacetylene ^d -[C ₄ H ₂] _∞ -	0.23, 0.10	4–31G	203 ± 4	21.9±0.4		
Polyyne ^e -[C ₂]-	0.22	3–21G	113.5 ± 1.5	23.3 ± 0.3		
All- <i>trans</i> polysilane ^f -[Si ₂ H ₄] _∞ -	0.0	6–31G	131.4±0.2	17.65 ± 0.03	72.5±0.1	7.7

^aSee Ref. 5 for the polarizability calculations and Ref. 37 for the geometry optimizations.

^bSee Ref. 33 for the polarizability calculations and Ref. 36 for the geometry optimizations.

See Ref. 33 for the polarizability calculations and the geometry optimizations.

^dSee Ref. 7 for the polarizability calculations and Ref. 38 for the geometry optimizations.

"See Ref. 9 for the polarizability calculations and Ref. 39 for the geometry optimizations.

^fSee Ref. 8 for the polarizability calculations and Ref. 40 for the geometry optimizations.

results (0.90, 0.65, and 0.89 for the x, y, and z components of the polarizability tensor, respectively) do not change significantly our improved estimates of the electric dipole polarizability per unit cell: $\alpha_{xx}/N=58.1$ a.u., $\alpha_{yy}/N=31.9$ a.u., $\alpha_{zz}/N=213.5$ a.u., $\overline{\alpha}/N=101.2$ a.u. as N tends to infinity.

F. Effect of the nature of the chain

Here we compare polythiophene with the most studied π -conjugated systems, polyacetylene, polyyne, and polydiacetylene, and with σ -conjugated polysilane. With the exception of the *trans-cisoïd* conformer of polyacetylene chains, all results have been reported in previous studies^{6-9,33} for which the geometrical parameters have been optimized.³⁶⁻⁴⁰ To isolate the effect of conformation on the polarizability of polyacetylene, bond length and bond angle values, optimized for the all-*trans* conformation either at the MP2 level with an extended basis set augmented with diffuse functions³⁶ or at the Hartree–Fock level using the 3-21G atomic basis set,³³ have been used to build the oligomers having the *trans-cisoïd* conformation.

To the best of our knowledge, we report in Table IV all *ab initio* coupled Hartree–Fock calculations of the polarizabilities of increasingly large conjugated chains. These values have been obtained after extrapolation of the polarizabilities to the infinite chain limit and have been computed with split-valence (3-21G, 4-31G, and 6-31G) and extended $(6-31G^*, 6-31G^{**}, and 6-31G+PD)$ atomic basis sets. The different sizes and shapes of the unit cells mean that we have to compare either the asymptotic values per unit length or per unit volume. We chose the α_{zz}/L and $\bar{\alpha}/V$ scales because they provide information about the relative 1D and 3D optical properties. The van der Waals exclusion volumes computed by the Connolly program⁴¹ are used as volume V. Bond length alternations which play an important role⁴ in the polarizable character of a compound, are also given. Polythiophene possesses a larger α_{r}/L value than both σ -conjugated polysilane and the π -conjugated polyyne and polydiacetylene, which have a strong alternating character due to the triple bonds where the electrons are localized. However, polythiophene is less polarizable than the all-trans and trans-cisoid conformers of polyacetylene. The analysis of the $\bar{\alpha}/V$ values confirms this feature. Once again, we stress the importance of the bond length alternation and the need to have correct Δr values for predicting the relative potential of different polymeric systems for optics applications. Our results demonstrate also that the all-trans conformation of polyacetylene chains ensures larger polarizabilities than the trans-cisoid conformation.

IV. STRUCTURE-POLARIZABILITY RELATIONSHIPS FOR POLYTHIOPHENE

A. Calculation of the band structure

In restricted Hartree–Fock theory, the many-electron wave functions of the closed-shell one-dimensional periodic systems are approximated by Slater determinants which



FIG. 4. 3-21G band structure of polythiophene.

are constructed from doubly occupied crystalline orbitals. These crystalline orbitals are single-particle states defined in the linear combination of atomic orbitals (LCAO) formalism by

$$\phi_n(k,\mathbf{r}) = \frac{1}{\sqrt{(2N+1)}} \sum_{j=-N}^{N} e^{ikja} \sum_{p=1}^{\omega} C_{pn}(k)$$
$$\times \chi_p(\mathbf{r} - \mathbf{R}_p - ja\mathbf{e}_z), \qquad (4)$$

where *n* and *k* are the band index and the wave vector or quasimomentum associated with the particle, respectively. (2N+1) is the (odd) number of unit cells considered $(N \rightarrow \infty)$ in the band structure calculation that corresponds also to the number of *k* states in one band or to the periodicity [(2N+1)a] of the crystalline orbitals imposed by the Born-von Karman cyclic boundary conditions. $1/\sqrt{2N+1}$ is then the normalization factor, *a* the unit cell length. The $C_{pn}(k)$ terms are the *k* dependent LCAO coefficients. $\chi_p(\mathbf{r}-\mathbf{R}_p-ja\mathbf{e}_z)$, is the *p*th atomic orbital centered in the *j*th unit cell. **e**_{*x*} is the unit vector in the period-



FIG. 5. Schematic representation of the topology of crystalline orbital $\phi_{42}(k=0)$ of polythiophene.

icity direction. The polymeric LCAO coefficients $C_{pn}(k)$ and their associated energies $\epsilon_n(k)$ are, respectively, the eigenvectors and eigenvalues of the matrix equation

$$\mathbf{F}(k)\mathbf{C}(k) = \mathbf{S}(k)\mathbf{C}(k)\boldsymbol{\epsilon}(k), \tag{5}$$

where F(k) and S(k) are the k-dependent Fock and overlap matrices. The standard theory of band structure calculations is described in several papers⁴² and is reviewed in two recent monographs.⁴³

B. SOS calculation of the polarizabilities per unit cell of polymers

Recently, we generalized the uncoupled Hartree–Fock molecular method to infinite periodic systems.¹⁷ In this procedure, the frequency-independent longitudinal polarizability per unit cell of infinite periodic systems is given by

$$\frac{\alpha_{zz}}{2N+1} = \frac{4a}{\pi} \sum_{a}^{\text{occ}} \sum_{r}^{\text{unocc}} \int_{0}^{\pi/a} \frac{|\Omega_{ar}(k)|^2}{\epsilon_r(k) - \epsilon_a(k)} dk, \qquad (6)$$

where the summations run over all the occupied (a) and unoccupied (r) bands. The integration over k points includes half the first Brillouin zone. The dipole transition strengths⁴⁴ between the crystalline orbitals $\phi_a(k)$ and $\phi_r(k), \Omega_{ar}(k)$, sometimes called oscillator strengths are defined in recent papers¹⁷ together with their antihermiticity property and a description of the analytical method used to compute them. Despite its neglect of reorganizational effects, this uncoupled Hartree-Fock method is adequate to obtain correct trends of asymptotic longitudinal polarizabilities per unit cell and qualitative agreement with the experimental data. Indeed, a recent study of the linear optical properties of polymers shows that the method not only reproduces the experimental trends but also provides an efficient way to analyze these properties in relation with the electronic structure of the infinite periodic systems.⁴⁵ Equation (7) explicitly shows that it is possible to decompose the total polarizability per unit cell into the contributions of each occupied band. Moreover, in each occupied Champagne, Mosley, and André: Polarizabilities of thiophenes

TABLE V. 3-21 G valence band contributions to the asymptotic longitudinal polarizability per unit cell (two thiophene rings) in atomic units. Crystalline orbitals of π symmetry are highlighted.

n	Contribution to α_{zz}/N
19	0.01
20	0.07
21	0.17
22	0.13
23	0.20
24	0.34
25	0.56
26	0.84
27	0.83
28	0.69
29	2.10
30	5.35
31	5.00
32	0.03 (π)
. 33	6.35
34	8.73
35	0.10 (π)
36	9.93
37	13.70
38	9.95
39	1.49 (π)
40	4.45 (π)
41	6.17 (π)
42	94,77 (π)

band, the contribution of the single-particle states may be followed as a function of the quasimomentum k

$$\frac{\alpha_{zz}}{(2N+1)} = \sum_{a}^{\infty} \alpha_{zz}(a),$$

$$= \sum_{a}^{\infty} \left\{ \int_{0}^{\pi/a} \alpha_{zz}(a,k) dk \right\},$$

$$= \sum_{a}^{\infty} \left\{ \int_{0}^{\pi/a} \left[\frac{4a}{\pi} \sum_{r}^{\operatorname{unocc}} \frac{|\Omega_{ar}(k)|^{2}}{\epsilon_{r}(k) - \epsilon_{a}(k)} \right] dk \right\}. \quad (7)$$

Thus it is possible to relate the topology and local polarizability of the band structure to each other. As presented in formula (7), such an analysis needs correct band indexing followed by correct band reordering in the cases where the bands cross. The band indexing is performed by looking at the gradients of the different bands which are computed according to a method due to André *et al.*⁴⁶

C. Band structure and longitudinal polarizability per unit cell of polythiophene

Using two thiophene rings as the translational unit cell of polythiophene, we performed the 3–21G band structure calculation of polythiophene with the PLH program.^{47,48} A particular feature of the PLH program consists in the inclusion of the long-range coulombic interactions which are accounted for via a multipole expansion technique including all the monopole–quadrupole and dipole–dipole interactions. The number of unit cells in the short and intermediate range regions are 7 and 13, respectively, in order to insure properly converging results. In the band structure calculation, we set the threshold for the two-electron inte-



FIG. 6. Schematic representation of the topology of crystalline orbital $\phi_{37}(k=\pi/a)$ of polythiophene.

grals at 10^{-7} a.u. The criterion for convergence on the density matrix elements is fixed at 10^{-5} . In the integration procedure which provides the longitudinal polarizability per unit cell, the number of k points in the first half Brillouin zone has been fixed at 21. The dispersion curves of the valence bands and the first unoccupied bands are represented in Fig. 4. They are labeled by a number which corresponds to the band ordering at k=0, i.e., from the deepest core levels to the last occupied valence bands.

Starting with these band structures, the asymptotic SOS longitudinal polarizabilities per subunit are computed using the method described above. The SOS asymptotic longitudinal polarizability per unit cell (two thiophene rings) is estimated to be 172.04 a.u. using the 3-21G atomic basis set, which is in close agreement with the value of 86.1 a.u. per thiophene ring extrapolated from the oligomeric calculations. With our aim to understand the origin of the large polarizability per unit cell of polythiophene in mind, we list the contributions of the valence bands to the total asymptotic longitudinal polarizability in Table V [cf. Eq. (7)]. The largest contributions come from the top of the highest occupied band, the crystalline orbitals of which have π symmetry. As illustrated in Fig. 5, the HOCO (highest occupied crystalline orbital) does not include any contributions from the sulfur atom and so, looks like an alternation of segments of HOCO of the all-trans and trans-cisoid polyacetylene. Therefore, the smaller polarizability of polythiophene compared to both forms of polyacetylene can be accounted for partly by the uneven shape of the carbon backbone of polythiophene with respect to the regular all-trans and trans-cisoid polyacetylene backbones. In addition, it is important in such a comparison to mention the aromaticity which, in order to stabilize the system, is known to reduce the polarizability of conjugated systems in which it is present. Such an interpretation is consistent with the results presented in the preceding section. The largest σ contribution comes from the crystalline orbitals of band 37 near the Brillouin zone edge which are represented in Fig. 6. As shown, this feature is due to σ conjugation that originates in the σ -conjugated segments formed by the sulfur atom with its two adjacent carbon atoms. The smaller contributions to the total polarizability per unit length of the σ -symmetry bands of polyfuran and polypyrrole, that we have recently shown,⁴⁹ highlight the important role played by the sulfur atoms in the formation of σ -conjugated segments.

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