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Theoretical investigation of the nonlinear optical properties of oligomers of polythienylenemethyldiene, a low band-gap material

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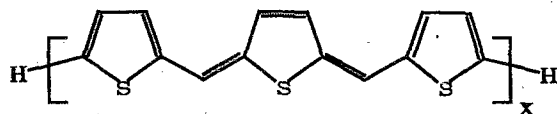
We present a theoretical investigation by the sum-over-states formalism of the static first- and third-order polarizabilities of thienylenemethyldiene oligomers; following the incorporation of a single conjugated carbon between the rings, these compounds present a partially quinoid geometry. We use a multireference determinant single-double configuration interaction approach to calculate excited-state energies, state dipole moments, and transition dipole moments which are introduced in the sum-over-states expressions. All the results are discussed in comparison to those obtained in thiophene oligomers of similar sizes; they indicate that the third-order polarizabilities are smaller for the methine-bridged compounds than for the corresponding thiophene oligomers. This feature is rationalized by analyzing the main optical (virtual excitation) channels that contribute to the nonlinear response.

I. INTRODUCTION

Much attention is given nowadays to the cubic nonlinear optical properties of conjugated polymers such as polydiacetylene, polyacetylene, or polythiophene, and their oligomers.¹⁻⁸ In particular, a large number of investigations seek to uncover the relationships among electronic structure, geometric structure, and nonlinear optical response.⁸⁻¹⁰ The motivation behind these studies is that conjugated polymers and oligomers appear to be excellent candidates for potential applications in optoelectronics and photonics.¹⁻¹⁰ It must be stressed that one of the main advantages of organics over inorganics is the ease with which organics can be chemically modified in order to optimize the response with respect to a given nonlinear optical process. In the context of such chemical engineering, theoretical investigations can prove useful in helping to select novel materials and providing guidelines towards synthesis and characterization efforts. Among novel organic materials with potentially large third-order nonlinear optical responses, low band-gap polymers and oligomers represent an interesting class of compounds to be analyzed, namely following the early work by Flytzanis and co-workers.¹¹ These authors derived an inverse relationship between the third-order susceptibility $\chi^{(3)}$ and the band-gap E_g of the material as $\chi^{(3)} \propto 1/E_g^6$.

Theoretical and experimental efforts¹²⁻¹⁸ have been directed towards the design of new polymeric materials with small band-gaps that could be intrinsically good electronic conductors. It has been shown that polypyrrole and polythiophene derivatives exhibit a significant band-gap decrease when quinoid contributions to the geometry are stabilized in the ground state. For instance, polyarylenemethyldienes have first been theoretically predicted to have band-gap values in the range 0.9–1.2 eV [Refs. 16(b) and 17]; subsequently, experimental data have confirmed these predictions;¹³ in addition, their nonlinear optical properties have been studied and appear to be interesting.^{18,19}

In the present work, we report the results of a theoretical study on the electronic components of the static first- and third-order polarizabilities (α and γ , respectively) for the 2,5-bis(2-thienylenemethyldiene)thiophene monomer and dimer



$x = 1, 2$

The monomer (dimer) containing two (four) aromatic rings and one (two) quinoid rings is denoted hereafter as *Th2a1q* (*Th4a2q*). These arylenemethyldiene oligomers, which are thus forced to present a partially quinoid geometry, have been recently synthesized.¹⁵ The $\chi^{(3)}$ response has been measured by degenerate four wave mixing (DFWM) at 700 nm and found to be on the order of 10^{-10} esu near resonance^{19(b)}; this classifies this kind of compound as potentially interesting for nonlinear optical applications. In order to analyze the effect of partially switching the geometry to a quinoid-like structure (following the incorporation of single conjugated carbons between the rings), our results are discussed in relation to those obtained on thiophene oligomers of similar sizes.²⁰

II. METHODOLOGY

The ground-state geometries of *Th2a1q* and *Th4a2q* are optimized by using the semiempirical Austin model 1 (AM1) technique.²¹ The geometry optimization of the largest oligomer *Th4a2q* and the α -heptathiophene oligomer *Th7a* are also carried out at the modified neglect of differential

overlap (MNDO) level.²² Note that, during the geometry optimizations, the oligomers are kept planar.^{16(b)} Both semiempirical techniques used are known to provide good geometry estimates in organic molecules. In the case of the thiophene-based molecules, the MNDO method yields a larger C α -C α inter-ring bond length and a larger degree of bond length alternation Δr (defined as the maximum difference between the length of a C-C bond inclined relative to the chain axis and a C-C bond parallel to the chain axis) along the chain. This will allow us to analyze the influence of the bond-length alternation on the nonlinear optical response.

On the basis of these geometries, the static components of the molecular polarizabilities α and γ are calculated via the sum-over-states (SOS) formalism²³ taking account of the 25 lowest excited states. The excitation energies and transi-

tion and state dipole moments to be introduced in the SOS expressions are evaluated by the intermediate neglect of differential overlap (INDO)/multireference determinant single- and double-excitation configuration interaction (MRD-SDCI) method²⁴ that we have described in detail previously²⁰ (we note that the Coulomb repulsion terms are expressed via the Ohno formula²⁵). We have chosen this approach because it has been used successfully to describe the electronic excitations and third-order nonlinear response in polyenes²⁶ and different thiophene oligomers;²⁰ in particular, the ordering of the lowest excited states and the evolution of γ with chain length were found to be in very good agreement with experiment.

Within the SOS approach, the α and γ tensor components, using a power series expansion, are expressed as

$$\alpha_{ij}(-\omega_\sigma; \omega_1) = \left(\frac{\hbar}{2\pi}\right)^{-1} \sum_{\text{perm}} \left[\sum_m \frac{\langle 0|\mu_i|m\rangle \langle m|\mu_j|0\rangle}{(\omega_{m0} - \omega_1 - i\Gamma_{m0})} \right],$$

$$\gamma_{ijkl}(-\omega_\sigma; \omega_1, \omega_2, \omega_3) = \frac{1}{6} \left(\frac{\hbar}{2\pi}\right)^{-3} \sum_{\text{perm}} \left[\sum_{m,n,p} \frac{\langle 0|\mu_i|m\rangle \langle m|\mu_j|n\rangle \langle n|\mu_k|p\rangle \langle p|\mu_l|0\rangle}{(\omega_{m0} - \omega_\sigma - i\Gamma_{m0})(\omega_{n0} - \omega_2 - \omega_3 - i\Gamma_{n0})(\omega_{p0} - \omega_3 - i\Gamma_{p0})} \right. \\ \left. - \sum_{m,n} \frac{\langle 0|\mu_i|m\rangle \langle m|\mu_j|0\rangle \langle 0|\mu_k|n\rangle \langle n|\mu_l|0\rangle}{(\omega_{m0} - \omega_\sigma - i\Gamma_{m0})(\omega_{n0} - \omega_3 - i\Gamma_{n0})(\omega_{n0} + \omega_2 - i\Gamma_{n0})} \right],$$

where $\langle 0|\mu_i|m\rangle$ is the electronic transition moment along the i th Cartesian axis for the molecule-fixed coordinate system between the ground state $|0\rangle$ and excited state $|m\rangle$; $\langle m|\mu_j|n\rangle$ denotes the dipole difference operator equal to $\langle m|\mu_j|n\rangle - \langle 0|\mu_j|0\rangle \delta_{mn}$; ω_{m0} (times \hbar) is the energy difference between state $|m\rangle$ and ground state $|0\rangle$; ω_1 , ω_2 , and ω_3 are the frequencies of the perturbing radiation fields; $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ is the polarization response frequency; Γ_{m0} is the damping associated to excited state $|m\rangle$; \sum_{perm} indicates a summation over the terms obtained by permuting the frequencies.

We emphasize that in this work we only deal with static polarizabilities. In this way, we can discuss the intrinsic nonlinear optical responses, which can be easily compared between sets of compounds (frequency-dependent values are indeed less comparable because of possible different resonance enhancements). The average values of α and γ discussed below are defined in terms of Cartesian tensor components as

$$\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3,$$

$$\langle \gamma \rangle = 1/5[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{zzxx})].$$

Here, we take the z axis to be the chain axis.

III. GEOMETRIC STRUCTURES

At first, we analyze at the semiempirical AM1 and MNDO levels the geometries of the fully aromatic *Th7a* and alternated aromatic/quinoid *Th4a2q* oligomers, whose mo-

lecular structures (and atom labeling) are presented in Fig. 1. We focus our attention on the longest oligomers as they are more representative of the polymers. The optimized AM1 and MNDO bond lengths for planar *Th7a* and *Th4a2q* are collected in Table I.

The comparison of the AM1 and MNDO geometries shows the following features:

(i) For the aromatic thiophene rings, the AM1 C α -C α inter-ring and C β -C β intraring bond lengths are found to be smaller than the MNDO values (for instance, in the *Th7a* central ring, these bonds, at the AM1 level, are shorter by 0.023 and 0.021 Å, respectively, with respect to the MNDO values); the two techniques lead to similar C α -C β bond-length values. As a consequence, the bond-length alternation is strongly enhanced when going from AM1 ($\Delta r \sim -0.03$ Å) to MNDO ($\Delta r \sim -0.06$ Å) geometry, which leads to a more pronounced aromatic character within the thiophene rings for the AM1-optimized geometry.

(ii) Within the quinoid segments introduced in the ground-state geometry, the MNDO-optimized single and double C-C bonds are longer than the AM1 ones, the Δr value being slightly increased from 0.10 Å in the AM1 geometry to 0.11 Å in the MNDO one.

To summarize, the results indicate a marked Δr increase in going from AM1 to MNDO geometry, especially for the aromatic thiophene rings. Note that in this case, the MNDO-calculated degree of bond-length alternation Δr (~ -0.06 Å) corresponds better to the experimental Δr value (~ -0.08 Å) from x-ray diffraction data on tetrathiophene.²⁶

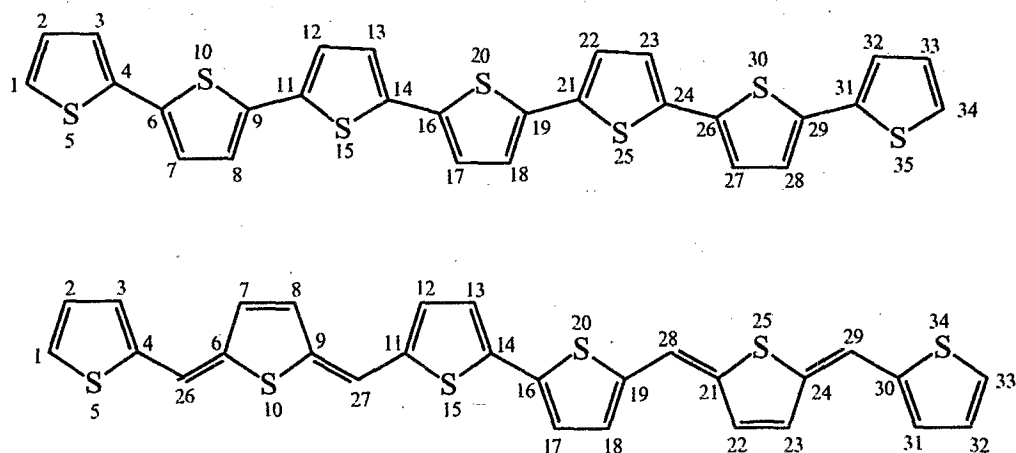


FIG. 1. Molecular structure and atom labeling of (top) the seven-ring thiophene oligomer *Th7a*; (bottom) the longer thienylenemethyldene oligomer *Th4a2q*.

IV. MOLECULAR POLARIZABILITIES

The static α and γ polarizabilities, calculated with the INDO/MRDCI/SOS method (on the basis of a power expansion of the electric field) are listed in Table II. We compare the average polarizabilities ($\langle\alpha\rangle$ and $\langle\gamma\rangle$) and the longitudinal components (α_{zz} and γ_{zzzz} , which totally dominate the $\langle\alpha\rangle$

TABLE I. Optimized AM1 and MNDO carbon-carbon and carbon-sulfur bond lengths (in Angstroms) for α -heptathiophene, *Th7a* and 2,5-bis(2-thienylenemethyldene)thiophene dimer *Th4a2q*.

	<i>Th7a</i>		<i>Th4a2q</i>	
	AM1	MNDO	AM1	MNDO
C1-C2	1.379	1.374	1.378	1.374
C2-C3	1.426	1.447	1.428	1.448
C3-C4	1.389	1.388	1.385	1.386
C1-S5	1.688	1.693	1.698	1.699
C1-S5	1.664	1.674	1.663	1.673
C4-C6	1.424	1.447
C4-C26	1.427	1.452
C6-C26	1.345	1.358
C6-C7	1.390	1.388	1.453	1.470
C7-C8	1.420	1.442	1.356	1.362
C8-C9	1.390	1.388	1.453	1.470
C6-S10	1.681	1.689	1.730	1.711
C9-S10	1.681	1.689	1.729	1.710
C9-C11	1.423	1.446
C9-C27	1.346	1.358
C11-C27	1.427	1.451
C11-C12	1.390	1.388	1.387	1.386
C12-C13	1.420	1.441	1.421	1.442
C13-C14	1.390	1.388	1.390	1.388
C11-S15	1.681	1.688	1.691	1.694
C14-S15	1.681	1.688	1.679	1.687
C14-C16	1.423	1.446	1.424	1.446
C16-C17	1.390	1.388
C17-C18	1.420	1.441
C16-S20	1.681	1.688

and $\langle\gamma\rangle$ responses) in the methine-bridged thiophene oligomers, to those in thiophene oligomers of similar sizes, i.e., the oligomers with three (*Th3a*), four (*Th4a*), six (*Th6a*), and seven (*Th7a*) thiophene rings. We also compare the polarizabilities obtained for *Th4a2q* and *Th7a* for two different input geometries AM1 and MNDO. In order to get a better idea of the intrinsic polarizabilities, we have scaled all the polarizability values by either the length of the conjugated framework l (defined as the distance between the most distant carbons) or the total number of π electrons n . Note that the molecular lengths of *Th2a1q* and *Th4a2q* (as represented by the l values) are approximately equal to those of *Th4a* and *Th7a*, respectively. Here also, we mostly discuss the longest oligomers *Th4a2q* and *Th7a* as they better represent the polymers.

We first focus on the results obtained on the basis of the AM1 geometries. As reported earlier,^{27,28} quinoid contributions to the geometry induce a significant enhancement in the longitudinal polarizability α_{zz} . In fact, we find a larger α_{zz} value in the *Th4a2q* oligomer, a 40 π -electron system, than for the seven-ring thiophene oligomer *Th7a* that contains two more π electrons 152×10^{-24} esu in *Th4a2q* vs 134×10^{-24} esu in *Th7a*. Therefore, if one were to consider the simple scaling laws relating γ to α values,²⁹ we would expect a very strong increase in the longitudinal component γ_{zzzz} as a consequence of introducing a quinoid character in the geometry. However, the trends observed for the third-order polarizabilities are totally different.

The thiophene oligomer *Th7a*, which is a totally aromatic system, presents the largest third-order response: the γ_{zzzz} value is equal to 2610×10^{-36} esu, a value to be compared to 1975×10^{-36} esu calculated for the methine-bridged *Th4a2q* oligomer. The γ_{zzzz} value in *Th4a2q* is actually closer to that calculated for the *Th6a* oligomer (1750×10^{-36} esu) that only contains 36 π electrons and is significantly less extended. A similar evolution of the different-order po-

TABLE II. INDO/MRD-SDCI/SOS static first- and third-order polarizabilities (expressed in 10^{-24} and 10^{-36} esu, respectively) of the two thienylenemethylydene oligomers and different thiophene oligomers calculated on the basis of the AM1 and, between parentheses, MNDO optimized geometries. The z axis is taken as the chain-length axis; n denotes the number of π electrons, l (expressed in Angstroms) represents the length of the conjugated framework (the distance between the most distant carbons).

	n	l	α_{zz}	$\langle\alpha\rangle$	$\langle\alpha\rangle/n$	$\langle\alpha\rangle/l$	γ_{zzzz}	$\langle\gamma\rangle$	$\langle\gamma\rangle/n$	$\langle\gamma\rangle/l$
<i>Th3a</i>	18	10.1	23.6	9.2	0.5	0.9	106.9	20.1	1.1	2.0
<i>Th2a1q</i>	20	12.3	37.7	12.9	0.6	1.1	189.3	37.6	1.9	3.1
<i>Th4a</i>	24	13.6	43.8	14.9	0.6	1.1	386.8	77.0	3.2	5.7
<i>Th6a</i>	36	21.6	103.8	34.7	1.0	1.6	1750	349.8	9.7	16.2
<i>Th4a2q</i>	40	26.0	151.8	50.9	1.3	2.0	1967	391.3	9.8	15.0
		(26.6)	(140.1)	(46.8)	(1.2)	(1.7)	(1269)	(253.8)	(6.3)	(9.5)
<i>Th7a</i>	42	25.5	133.9	44.8	1.1	1.8	2616	520.6	12.4	20.4
		(25.7)	(109.1)	(36.4)	(0.9)	(1.4)	(1442)	(286.4)	(6.8)	(11.1)

larizabilities is observed for the shorter oligomers; here also the scaled $\langle\alpha\rangle$ and $\langle\gamma\rangle$ polarizabilities reveal larger intrinsic first-order polarizabilities for the methine-bridged oligomer, while the third-order components are 1.4 to 1.8 times smaller than those in the thiophene oligomers.

The chain-length dependence of $\langle\gamma\rangle$ can be described with a simple power law

$$\gamma \propto N^a.$$

It has been described in detail for the thiophene oligomers,²⁰ where we calculate the a exponent to be equal to 3.42 when going from *Th4a* to *Th7a*. Between the thienylenemethylydene oligomers *Th2a1q* and *Th4a2q*, we obtain an exponent of 3.38. So, the chain-length evolutions of $\langle\gamma\rangle$, between *Th2a1q* and *Th4a2q* and between *Th4a* and *Th7a*, are nearly equal; this feature is consistent with the similar molecular extensions (l values) calculated for *Th2a1q* and *Th4a*, and for *Th4a2q* and *Th7a*.

Using the MNDO geometries as input leads to the same variations in the calculated polarizabilities (see Table II). With the introduction of quinoid moieties in the ground state, we observe an increase for the first-order polarizabilities (α_{zz} is equal to 140×10^{-24} esu in *Th4a2q* vs 109×10^{-24} esu in *Th7a*), but a reduction for the third-order polarizabilities (γ_{zzzz} goes from 1442×10^{-36} esu for *Th7a* to 1269×10^{-36} esu for *Th4a2q*). An interesting feature is the significant decrease in polarizability values when going from AM1 to MNDO input geometries, in particular, for the γ values which are more affected by the geometry modifications; with the MNDO input geometry, the α_{zz} (γ_{zzzz}) value for *Th7a* is lowered by 25×10^{-24} esu (1174×10^{-36} esu), while it shows a decrease of 12×10^{-24} esu (698×10^{-36} esu) for *Th4a2q*. This is due to the marked increase in bond-length alternation degree for the MNDO geometry, as previously discussed. The large geometry modifications within the aromatic thiophene rings when going from AM1 to MNDO geometry result in lowering much more the polarizabilities for the *Th7a* compound and tend thus to increase (reduce) the differences in α (γ) values calculated for *Th7a* and *Th4a2q*.

Therefore, it clearly appears that the switch from a purely aromatic structure (for instance, a thiophene oligomer) to an alternating fully quinoid/aromatic structure is *not* the right move to boost the γ values; actually, the introduction of a strong alternating aromatic/quinoid character

(which translates into large bond-length alternations) along the conjugated framework is detrimental to the γ values. We note that the same conclusions can also be taken from the results of recent *ab initio* calculations that we have carried out on several benzene and thiophene derivatives in either purely aromatic or quinoid geometric structures.³⁰

In order to rationalize the differences in the cubic nonlinear optical properties of thiophene and thienylenemethylydene oligomers, we have examined the main couplings among the singlet states. In this way, we can determine the principal optical (virtual-excitation) channels that dominate the nonlinear response, i.e., that contribute primarily to the γ value. We first discuss the results obtained on the basis of the AM1-optimized geometries. As in the case of polyenes³¹⁻³³ and thiophene oligomers,²⁰ the $1A_g$ ground state is most strongly coupled to the $1B_u$ excited state, which is dominated by the highest-occupied molecular orbital \rightarrow lowest-unoccupied molecular orbital (HOMO \rightarrow LUMO) singly excited configuration (the transition dipole moments between the $1B_u$ state and the ground state are equal to 9.7 and 16.9 D in *Th2a1q* and *Th4a2q*, respectively). A few higher-lying A_g excited states, denoted mA_g , exhibit significant transition dipole moments with the $1B_u$ state. For *Th2a1q*, the mA_g states correspond to the $6A_g$ and $7A_g$ states, located 5.67 and 5.81 eV above the ground state, respectively, and to a smaller extent, the $5A_g$ state at 5.19 eV. For *Th4a2q*, the dominant mA_g states are the $6A_g$ (at 4.62 eV) and $7A_g$ (at 4.79 eV) states; other contributing states are the $4A_g$ (at 3.98 eV) and $5A_g$ (at 4.25 eV) states. In comparison to thiophene chains of similar sizes,²⁰ there occurs in the methine-bridged oligomers an increase in the number of A_g states which play an important role in the third-order nonlinear response. In addition, higher-lying B_u states (denoted nB_u states) contribute to $\langle\gamma\rangle$, especially for the longest oligomer *Th4a2q*. The dominant nB_u states (the $3B_u$ state at 4.06 eV and the $5B_u$ at 4.56 eV) also present significant transition dipole moments with the ground state (4.9 and 3.3 D, respectively; the corresponding values are 3.9 and 0.8 D for the thiophene oligomer *Th7a*). These states are involved in negatively contributing channels of the type $1A_g \rightarrow 1B_u \rightarrow 1A_g \rightarrow nB_u \rightarrow 1A_g$ that contribute much more to decrease the γ_{zzzz} value in *Th4a2q* than in the case of *Th7a*, where the $5B_u$ state is more weakly coupled to the ground state. Moreover, the $5B_u$ state

TABLE III. INDO/MRD-SDCI/SOS static chain-axis γ_{zzz} components (in 10^{-36} esu) arising from different virtual-excitation channels in *Th4a2q* and *Th7a* on the basis of the AM1- and MNDO-optimized geometries.

	<i>Th4a2q</i>	<i>Th7a</i>	<i>Th4a2q</i>	<i>Th7a</i>
	AM1 geometry		MNDO geometry	
(i) $1A_g \rightarrow 1B_u \rightarrow mA_g \rightarrow 1B_u \rightarrow 1A_g$	7300	6779	5645	4059
(ii) $1A_g \rightarrow 1B_u \rightarrow 1A_g \rightarrow 1B_u \rightarrow 1A_g$	-4941	-4169	-3955	-2492
(i) + (ii)	2359	2610	1690	1567
(iii) All channels	1967	2616	1269	1450

in *Th4a2q* is strongly coupled to the $2A_g$ and mA_g states and is involved in channels such as $1A_g \rightarrow 1B_u \rightarrow mA_g \rightarrow nB_u \rightarrow 1A_g$, which also provide negative contributions to γ_{zzz} .

In the case of the MNDO input geometries, because of the larger bond-length alternation, the transition energies are calculated to be higher. For instance, the mA_g states in *Th4a2q* are calculated to be located at 3.58 eV ($3A_g$), 4.17 eV ($4A_g$), 4.43 eV ($5A_g$), 4.80 eV ($6A_g$), or 4.89 eV ($7A_g$). Also, even though the number of A_g states which contribute to the third-order polarizabilities tends to increase, their transition dipole moments with the $1B_u$ state decrease significantly. As a result, the weaker couplings of the mA_g states with the $1B_u$ excited state and the higher transition energies calculated on the basis of the MNDO-optimized geometry concur to provoke a strong decrease of the γ values with respect to those calculated with the AM1-optimized geometries. Moreover, the number of B_u states involved in channels that provide negative contributions to γ_{zzz} and the corresponding transition dipole moments with the mA_g states increase, which contributes to reduce the MNDO-geometry γ values still further. For *Th4a2q*, the dominant higher-lying nB_u states presenting significant transition dipole moments with the ground state correspond to the $3B_u$ state located at 4.17 eV, the $4B_u$ state located at 4.71 eV, and the $5B_u$ state located at 4.76 eV; they present transition dipole moments with the ground state of 4.9, 2.8, and 1.4 D, respectively. For *Th7a*, they correspond to the $2B_u$ state at 3.70 eV, the $3B_u$ state at 4.13 eV, and the $5B_u$ state at 4.92 eV; these present smaller transition dipole moments with the ground state (1.7, 4.4, and 0.9 D, respectively) with respect to those calculated for *Th4a2q*.

In order to illustrate the major contributions of these excited states to the static third-order polarizabilities of the thienylenemethylidene and thiophene oligomers, we present in Table III the contributions to the static chain-axis component γ_{zzz} in *Th4a2q* and *Th7a*, arising from (i) the positive $1A_g \rightarrow 1B_u \rightarrow mA_g \rightarrow 1B_u \rightarrow 1A_g$ channels [Fig. 2(a)]; (ii) the negative $1A_g \rightarrow 1B_u \rightarrow 1A_g \rightarrow 1B_u \rightarrow A_g$ channel [Fig. 2(b)]; and (iii) all the channels. We point out that adding cases (i) and (ii) would correspond to a three-state-like model contribution for γ_{zzz} .^{9,10(a),34,35} By summing all the positive terms involved in case (i) for the mA_g states, we obtain on the basis of an AM1 (MNDO) geometry a contribution to γ_{zzz} of $+7300 \times 10^{-36}$ esu ($+5645 \times 10^{-36}$ esu) in *Th4a2q* vs $+6779 \times 10^{-36}$ esu ($+4059 \times 10^{-36}$ esu) in *Th7a*, i.e., a difference of $+521 \times 10^{-36}$ esu ($+1586 \times 10^{-36}$ esu). The larger

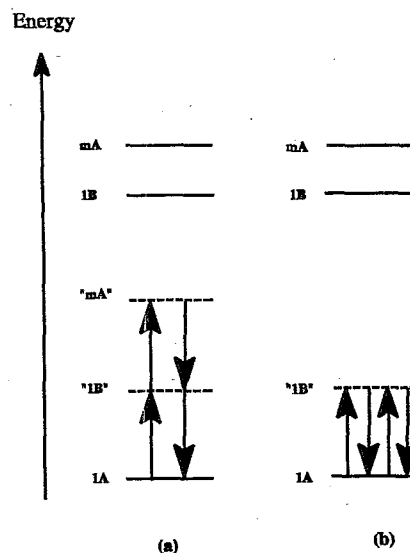


FIG. 2. An illustration of the two types of virtual-excitation channels contributing to γ in the context of the three-state model. The states between quotes refer to the primary stationary state contributing to a given virtual state; the states without quotes represent the real states of the molecule (A denotes an A_g state and B denotes a B_u state).

contribution obtained in *Th4a2q* is essentially due to a stronger coupling of the $1B_u$ excited state with the mA_g state and the ground state. However, that very same coupling leads to a very large negative $1A_g \rightarrow 1B_u \rightarrow 1A_g \rightarrow 1B_u \rightarrow 1A_g$ contribution in *Th4a2q*: -4941×10^{-36} (-3955×10^{-36}) vs -4169×10^{-36} esu (-2492×10^{-36} esu) in *Th7a*, i.e., a difference of -772×10^{-36} esu (-1463×10^{-36} esu).

The three-state-like model for the third-order polarizability thus provides γ_{zzz} values on the order of $+2359 \times 10^{-36}$ esu ($+1690 \times 10^{-36}$ esu) for the *Th4a2q* oligomer and $+2610 \times 10^{-36}$ esu ($+1567 \times 10^{-36}$ esu) for the *Th7a* oligomer. We observe that, in the *Th7a* case, there is good agreement between the three-state model and the fully converged γ_{zzz} values (contributions arising from channels including the nB_u and $2A_g$ excited states thus mostly cancel each other). On the contrary, for the thienylenemethylidene oligomer, the converged γ_{zzz} value $+1967 \times 10^{-36}$ esu ($+1269 \times 10^{-36}$ esu) is significantly lower than that provided by the three-state model; in this case, channels involving the nB_u , $2A_g$, and mA_g excited states are found to contribute to decrease significantly the γ_{zzz} value. Hence, even if the dominant states which contribute to the nonlinear optical response of the thienylenemethylidene oligomers are by and large the same as those in the thiophene oligomers, we observe that the larger coupling of the $1B_u$ excited state with the ground state and contributions from the nB_u states lead to lower γ values in the thienylenemethylidene oligomers.

V. SYNOPSIS

The evaluation of the nonlinear optical properties of thienylenemethylidene oligomers (the *Th2a1q* monomer and the *Th4a2q* dimer) using the sum-over-states formalism

and the comparison with the results obtained for thiophene oligomers of similar sizes show that the switch from an aromatic structure to an alternating aromatic/quinoid structure does *not* increase the third-order polarizability $\langle\gamma\rangle$. Actually, even if the chain-length evolution of $\langle\gamma\rangle$ is similar for both types of compounds, the $\langle\gamma\rangle$ values are calculated to be smaller in the methine-bridged compounds than in the corresponding thiophene oligomers. We also obtain that the third-order polarizabilities are significantly enhanced when less bond-alternated geometries are considered.

An analysis of the major virtual-excitation channels that are involved in the nonlinear optical response allows us to rationalize these results. When considering a three-state-like model based on the $1A_g$, $1B_u$, and mA_g states, we find that the contributions to the γ_{zzzz} value for the thienylenemethylidene chains are quite similar than for the corresponding thiophene oligomers. However, in the *Th4a2q* oligomer, the importance of the channels including higher-lying nB_u states as well as the $2A_g$ and mA_g states (which provide a net negative contribution to the nonlinear optical response) increases; these contributions are weaker for the thiophene oligomers due to the smaller transition moments between these B_u states and the ground state.

It is informative to analyze the results of our work in the context of the elegant theoretical and experimental investigations recently performed by Marder and co-workers on the molecular polarizabilities of linear polymethine dyes.^{9,10(a),36} Although the thienylenemethylidene and thiophene oligomers are not polymethine chains *stricto sensu*, to a good first approximation, their conjugated carbon backbone can be considered to be that way. Marder *et al.* have demonstrated that neutral polymethines can be driven from a polyene-like structure (associated to a relatively large band-gap) to a more cyanine-like structure (associated to a smaller band-gap), for instance, upon application of an external electric field or upon substitution by strong donor and acceptor groups;^{9,37} moreover, Meyers *et al.*^{10(a)} have shown on theoretical grounds that, as the structure becomes more cyanine-like, the absolute contributions to γ_{zzzz} from the negative optical channels increase much faster than those from the positive channels. This is the situation we observe here when we compare thienylenemethylidene and thiophene oligomers, the switch to an alternating aromatic/quinoidic structure leading to a smaller band-gap. This suggests that, if the thienylenemethylidene oligomers were end capped by strong donors and acceptors, very large negative γ values could be obtained.

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