

Research Article

Second Harmonic Generation, Electrooptical Pockels Effect, and Static First-Order Hyperpolarizabilities of 2,2'-Bithiophene Conformers: An HF, MP2, and DFT Theoretical Investigation

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The static and dynamic electronic (hyper)polarizabilities of the equilibrium conformations of 2,2'-bithiophene (*anti-gauche* and *syn-gauche*) were computed in the gas phase. The calculations were carried out using Hartree-Fock (HF), Møller-Plesset second-order perturbation theory (MP2), and density functional theory methods. The properties were evaluated for the second harmonic generation (SHG), and electrooptical Pockels effect (EOPE) nonlinear optical processes at the typical $\lambda = 1064$ nm of the Nd:YAG laser. The *anti-gauche* form characterized by the S-C₂-C_{2'}-S dihedral angle of 137° (MP2/6-311G**) is the global minimum on the potential energy surface, whereas the *syn-gauche* rotamer (S-C₂-C_{2'}-S = 48°, MP2/6-311G**) lies ca. 0.5 kcal/mol above the *anti-gauche* form. The structural properties of the *gauche* structures are rather similar to each other. The MP2 electron correlation effects are dramatic for the first-order hyperpolarizabilities of the 2,2'-bithiophenes, decreasing the HF values by ca. a factor of three. When passing from the *anti-gauche* to the *syn-gauche* conformer, the static and frequency-dependent first-order hyperpolarizabilities increase by ca. a factor of two. Differently, the electronic polarizabilities and second-order hyperpolarizabilities of these rotamers are rather close to each other. The *syn-gauche* structure could be discriminated from the *anti-gauche* one through its much more intense SHG and EOPE signals.

1. Introduction

Thiophene-based oligomers and polymers are an interesting class of π -conjugated materials for the development and construction of conductive and nonlinear optical (NLO) devices [1–5]. Electronic properties of π -conjugated polymeric systems are significantly affected by the twisting degree of the backbone and extension of the electron delocalization although molecular structure and physicochemical properties of extended oligomers and polymers are usually modelled through smaller oligomeric chains [6, 7].

The C _{α} -C _{α'} bonded bithiophene oligomer, 2,2'-bithiophene (Figure 1), is the principal building block of polythiophene chains, extensively characterized by experimental and theoretical studies. In the solid state, 2,2'-bithiophene predominantly exists as a planar *anti*-structure together with a nonnegligible fraction of planar *syn*-conformation (ca. 15%) [8]. A slightly different picture occurs in the gas phase: two nonplanar minimum-energy structures are observed to

coexist (Figure 1), which are characterized by S-C₂-C_{2'}-S dihedral angles of $148^\circ \pm 3^\circ$ (*antigauche*) and $36^\circ \pm 5^\circ$ (*syngauche*) [9]. On the basis of electron diffraction data [9] and experimental fluorescence spectra [10], the *anti-gauche* is the minimum-energy form on the potential energy surface of the 2,2'-bithiophene, being more stable than the *syngauche* rotamer by 1.16 ± 0.13 kcal/mol (enthalpy difference extrapolated from the dependence of the relative abundance in the 58–130°C range of temperatures) [10] and 0.18 kcal/mol at 100°C (energy difference) [9]. On the theoretical side, there are many contributions in the literature about relative stabilities and torsional potentials of 2,2'-bithiophene conformations [11–15]. In agreement with experiment, correlated *ab initio* and density functional theory (DFT) levels concordantly predict both the *gauche* structures as stationary points on the PESs of 2,2'-bithiophene, the *anti-gauche* being predicted to be the global minimum [11–15]. The torsional potentials for the rotation around the C₂-C_{2'} bond

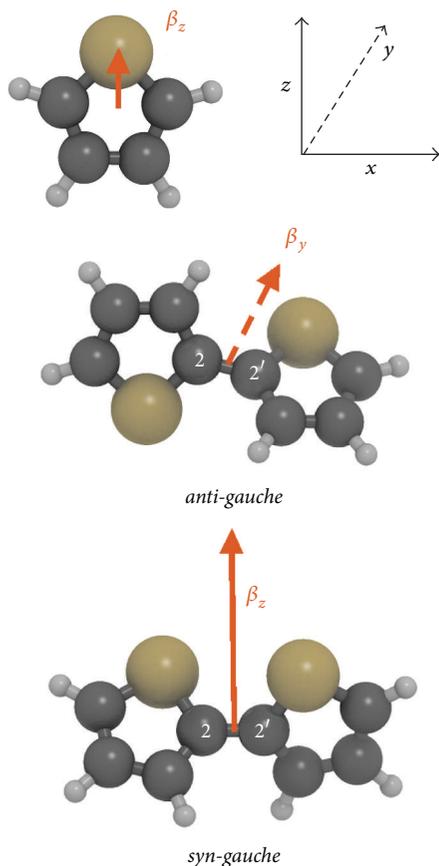


FIGURE 1: Structures of thiophene and 2,2'-bithiophene rotamers. Colours: white (hydrogen), grey (carbon), and orange (sulphur).

are characterized by flat double-well potentials, allowing a high degree of conformational flexibility to oligothiophenes [11–15]. In addition, the influence of the torsional potential on the electronic polarizabilities of 2,2'-bithiophene rotamers was analyzed by Lukeš et al. [14] using HF/aug-cc-pVDZ and MP2/aug-cc-pVDZ computations. However, the average electronic polarizabilities of 2,2'-bithiophene are little affected by the conformation, varying within 5–6% [14]. Therefore, this response electric property is little informative for identification of conformations. On the other hand, electronic first-order hyperpolarizabilities (β), the related NLO electrooptical Pockels effect (EOPE), and second harmonic generation (SHG) properties are usually much more influenced by structural characteristics than electronic polarizabilities, being of potential utility for discrimination of conformers [16–19].

In the present investigation, we have calculated the static and dynamic electronic (hyper)polarizabilities of the most stable conformations of 2,2'-bithiophene in the gas phase, aiming to identify physicochemical properties useful to discriminate the different rotamers. The frequency-dependent first-order hyperpolarizabilities were obtained for the SHG and EOPE NLO processes at the typical experimental wavelength of the Nd:YAG laser (1064 nm). Neither experimental nor theoretical electronic β values of 2,2'-bithiophenes are known so far, whereas some computational studies were previously carried out on the first-order hyperpolarizabilities of the monomer of thiophene [20–25].

2. Computational Details

The geometries of the *anti-gauche* and *syn-gauche* 2,2'-bithiophene rotamers (Figure 1) were optimized using *ab initio* Hartree-Fock (HF) and Møller-Plesset second-order perturbation theories (MP2) with the 6-311G** basis set. The vibrational analysis obtained under the harmonic approximation confirmed that all the investigated structures are stationary points (no imaginary frequencies). The calculations were also carried out on the thiophene molecule for comparison.

For thiophene and 2,2'-bithiophenes, we computed the dipole moments (μ), static and dynamic electronic polarizabilities (α), first-order hyperpolarizabilities (β), and second-order hyperpolarizabilities (γ). To this purpose, the HF and MP2 levels as well as a series of hybrid DFT methods such as B3LYP [26, 27], PBE0 [28], BH&HLYP [26], and B97-1 [29] were employed. Additionally, we investigated the performances of the long-range corrected ω B97X-D functional [30], recently employed with success for response electric property calculations [31–34]. The present computations were thoroughly carried out using the polarised and diffuse Sadlej's POL basis set [35]. There are many indications in the literature showing that this basis set is adequate for predicting response electric properties of organic compounds [31, 36–39]. However, for thiophene as a test case, we also performed (hyper)polarizability calculations using the larger correlation-consistent Dunning's triple-zeta basis set (aug-cc-pVTZ) [40]. At the HF level, the static α and β values were determined analytically by means of the coupled-perturbed HF (CP-HF) theory [41, 42], whereas the MP2 and DFT α and β data were obtained through a finite-field (FF) numerical scheme illustrated in detail by Kurtz and coworkers [43]. For the FF computations, we used a field strength amplitude of 0.005 a.u.. The accuracy of the numerical procedure was verified at the HF level by comparing the FF-HF and CP-HF (hyper)polarizability values. The static γ values were determined at the HF/POL level by means of the FF procedure. Frequency-dependent polarizabilities [$\alpha(-\omega; \omega)$] and first-order hyperpolarizabilities were computed for the 2,2'-bithiophenes by using the CP-HF procedure at the characteristic Nd:YAG laser wavelength (λ) of 1064 nm ($\hbar\omega = 0.04282$ a.u.). Specifically, the SHG [$\beta(-2\omega; \omega, \omega)$] and EOPE [$\beta(-\omega; \omega, 0)$] NLO processes were investigated. At this λ value, resonance enhancement effects for the SHG phenomenon are expected to be rather negligible, since the $2\hbar\omega$ value of 0.08564 a.u. (2.33 eV) is rather far from the lowest-energy absorption of planar 2,2'-bithiophene which is observed in gas at 3.86 eV [44, 45].

As commonly used in the literature, the calculated physicochemical properties are here expressed as dipole moment (μ), average polarizability ($\langle\alpha\rangle$), polarizability anisotropy ($\Delta\alpha$), first-order hyperpolarizability aligned along the μ direction (β_μ), and average second-order hyperpolarizability ($\langle\gamma\rangle$), which are orientationally invariant quantities:

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2},$$

$$\langle\alpha\rangle = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}),$$

$$\Delta\alpha = \left\{ \frac{1}{2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{yz}^2) \right] \right\}^{1/2},$$

$$\beta_\mu = \frac{\sum_{i=x,y,z} \beta_i \mu_i}{|\mu|}, \quad (1)$$

where β_i ($i = x, y, z$) is given by $\beta_i = (1/3) \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji})$

$$\langle \gamma \rangle = \frac{1}{5} (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}). \quad (2)$$

For the (hyper)polarizabilities, atomic units are used throughout the work. Conversion factors to the SI are 1 a.u. of α ($e^2 a_0^2 E_h^{-1}$) = $1.648778 \times 10^{-41} \text{ C}^2 \text{ m}^2 \text{ J}^{-2}$; 1 a.u. of β ($e^3 a_0^3 E_h^{-2}$) = $3.206361 \times 10^{-53} \text{ C}^3 \text{ m}^3 \text{ J}^{-2}$; 1 a.u. of γ ($e^4 a_0^4 E_h^{-3}$) = $6.235377 \times 10^{-65} \text{ C}^4 \text{ m}^4 \text{ J}^{-3}$. All calculations were performed using the GAUSSIAN 09 program [46].

3. Results and Discussion

3.1. Geometries and Energetics of Thiophene and 2,2'-Bithiophene Rotamers. The structural parameters of the equilibrium conformations of 2,2'-bithiophene (*anti-gauche* and *syn-gauche*) as well as those of the monomer obtained in the gas phase at the MP2/6-311G** level are displayed in Figure 2. On the basis of the MP2/6-311G** calculations, the *anti-gauche* form is the global minimum, while the *syn-gauche* form is less stable by $0.51 \text{ kcal}\cdot\text{mol}^{-1}$, in excellent agreement with previous correlated *ab initio* results [11–15] and in particular with the highest CCSD(T)/6-31G** and CCSD(T)/cc-pVDZ levels ($0.49 \text{ kcal}\cdot\text{mol}^{-1}$) [13]. Thus following the MP2/6-311G** results, the *anti-gauche* rotamer is the prevailing form of 2,2'-bithiophene in vacuum (ca. 70%), the *syn-gauche* being, however, an important conformation (ca. 30%).

The MP2/6-311G** geometry of thiophene is in good agreement with the experimental gas phase microwave structure [47]. In particular, the experimental C–S, C–C, and C=C bond lengths are well reproduced by the present computations. As can be appreciated from the data reported in Figure 2, the agreement between the observed [9] and calculated geometries for the 2,2'-bithiophene is slightly less satisfactorily. In particular, the present computations underestimate the experimental typical S–C₂–C_{2'}–S dihedral angle (148°) by 11° and the C–C interring bond length (1.46 Å) by ca. 0.01 \AA . However, the MP2/6-311G** S–C₂–C_{2'}–S dihedral angles of 137° (*anti-gauche* rotamer) and 48° (*syn-gauche* rotamer) are in reasonable agreement with the CCSD(T)/6-31G* estimates (142° and 44° , resp.) [13]. Some additional observations can be made: (i) the equilibrium geometry of the thiophene ring shows only little differences when passing from the monomer to the dimer; (ii) the geometries of the *gauche* conformations are very similar to each other. Indeed,

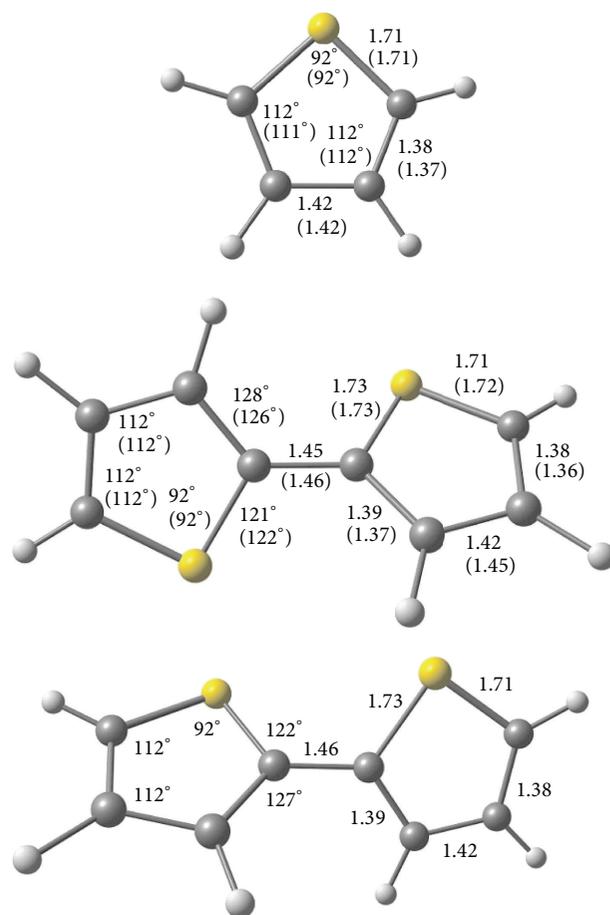


FIGURE 2: Gas phase MP2/6-311G** geometrical parameters of thiophene and 2,2'-bithiophene *anti-gauche* and *syn-gauche* rotamers. The experimental data reported in parentheses are taken from [47] (thiophene) and [9] (2,2'-bithiophene). The MP2/6-311G** (experimental) S–C₂–C_{2'}–S dihedral angles are 137° (148° , see [9]) and 48° for the *anti-gauche* and *syn-gauche* conformation, respectively.

the bond lengths and angles of the *anti-gauche* rotamer differ, respectively, by no more than 0.01 \AA and 1° from the data of the *syn-gauche* form.

3.2. Effects of the Basis Set and Theoretical Level on the Electronic (Hyper)polarizabilities of Thiophene. As widely documented in the literature, accurate estimates of electronic (hyper)polarizabilities need polarized and diffuse basis sets as well as introduction of electron correlation contributions [48–52]. In particular for the series of thiophene ($\text{C}_4\text{H}_4\text{X}$, X = O, S, Se, Te) [23] and pyrrole ($\text{C}_4\text{H}_4\text{YH}$, Y = N, P, As, Sb, Bi) [53] homologues, the correlated MP2 method reproduces reasonably well the response electric properties obtained using high-level CCSD(T) and MP4-SDTQ calculations. In the current study, we explored the effects of the basis set and computational method on the μ , α , and β values of thiophene as a case test, for which some experimental and high-level theoretical data are known. Specifically, we compared the POL and the aug-cc-pVTZ basis sets. The POL basis set consists of [3s2p] functions for hydrogen atom, [5s3p2d] for carbon and [7s5p2d] for sulphur, giving a total of 164 basis

TABLE 1: Dipole moments (D), static electronic polarizabilities (a.u.), and first-order hyperpolarizabilities (a.u.) of thiophene^a.

	HF ^b	MP2	BH and HLYP	PBE0	B3LYP	B97-1	ω B97X-D	MP4-SDTQ ^c	Exp.
μ_z	0.69 (0.70)	0.42	0.53	0.49	0.46	0.48	0.52	0.70	0.55 ^d
α_{xx}	68.61 (68.69)	71.49	7019	71.04	72.18	71.86	70.63	68.32	
α_{yy}	44.37 (44.51)	45.17	43.81	43.77	44.48	44.35	44.25	44.61	
α_{zz}	75.81 (76.00)	76.84	76.43	76.95	78.02	77.68	76.79	75.50	
$\langle\alpha\rangle$	62.93 (63.07)	64.50	63.48	63.92	64.89	64.62	63.89	62.81	60.71 ^e ; 64.90 ^f ; 65.17 ^g ; 66.12 ^h
$\Delta\alpha$	28.52 (28.54)	29.36	29.99	30.66	31.03	30.83	29.94	27.99	23.25 ^e ; 31.90 ^f ; 21.56 ^g
β_{xxz}	-5.2 (-1.7)	-1.7	-1.2	1.7	2.2	2.9	-0.8	-5.1	
β_{yyz}	6.2 (7.3)	9.4	9.9	12.8	12.6	12.3	9.7	10.9	
β_{zzz}	40.4 (40.5)	4.5	28.3	26.8	25.1	26.8	30.8	7.7	
β_μ	41.3 (46.1)	12.2	37.0	41.3	39.9	42.0	39.7	13.5	

^aThe calculations were performed with the POL basis set on the MP2/6-311G** geometries.

^bThe values in parentheses refer to the HF/aug-cc-pVTZ computations.

^cValues taken from [23]. Basis set: 6-31G (3d) + pd.

^dReference [55].

^eReference [56].

^fReference [57].

^gReference [58].

^hReference [59].

functions on thiophene, which are ca. half of the functions for the aug-cc-pVTZ basis set ([4s3p2d] for H, [5s4p3d2f] for C, and [6s5p3d2f] for S). The calculations were performed at the HF level and the data are collected in Table 1. The results show that, when passing from the HF/POL to HF/aug-cc-pVTZ level, only marginal variations are observed on the calculated properties. Indeed, the μ , $\langle\alpha\rangle$, $\Delta\alpha$, and β_μ values vary by 1.43, 0.22, 0.04, and 10.41%, respectively. It is worth mentioning that the above results are in line with previous (hyper)polarizability studies using the two basis sets [22, 31, 54]. However, it is important to notice that for thiophene the HF/aug-cc-pVTZ hyperpolarizability computations require a CPU demand by one order of magnitude greater than that for the HF/POL calculations. Thus, the use of the POL basis set can be considered a valid compromise between accuracy and computational cost and will be entirely adopted for the subsequent MP2 and DFT calculations on thiophene and on the 2,2'-bithiophenes.

The effects of electron correlation as evaluated at the MP2/POL level are rather significant for the dipole moment but negligible for the polarizabilities, decreasing the HF/POL μ datum by ca. 0.3 D (-40%) and increasing the $\langle\alpha\rangle$ value by ca. 2.5% and the $\Delta\alpha$ value by ca. 2.9%. All the DFT methods give similar μ and α values to each other, being in reasonable agreement with the MP2/POL data. The observed gas phase dipole moment of 0.55 D [55] is underestimated by the MP2 and DFT calculations (by 0.03–0.13 D), the smallest deviation being obtained by the ω B97X-D functional. The experimental $\langle\alpha\rangle$ ($\Delta\alpha$) data, comprised between 61 and 66 a.u. (23 and 32 a.u.) [56–59], are reasonably well reproduced by all the present theoretical methods, including the HF level. More importantly, the introduction of electron correlation contributions is crucial for the first-order hyperpolarizability. In fact, when passing from the HF/POL to MP2/POL level, the β_μ value reduces by ca. a factor of three. The effect

is especially conspicuous for the β_{zzz} component, which decreases by one order of magnitude. Note that our HF versus MP2 comparison for thiophene agrees with those previously obtained with other basis sets [22, 23]. Unfortunately, the experimental first-order hyperpolarizability of thiophene is not available so far. However, it is of interest mentioning that the present MP2/POL β_μ (thiophene) value is in good agreement with the datum previously predicted by the high-level MP4-SDTQ calculations ($\beta_\mu = 13.5$ a.u.) [23], showing a difference of 1.3 a.u. (-9.6%). On the other hand, similar to the HF/POL computations, all the DFT methods overestimate the MP2/POL β_μ value by a factor between 3.0 and 3.4, the BH&HLYP functional giving the closest value. Note that the failure of the traditional DFT methods in the prediction of the electronic (hyper)polarizabilities especially of π -conjugated compounds is well known and has been exhaustively illustrated by Champagne and co-workers [60]. Quite surprisingly, it is worth noting that the use of the long-range corrected ω B97X-D functional does not improve significantly the performances obtained using the conventional functionals.

3.3. Static and Frequency-Dependent (Hyper)polarizabilities of 2,2'-Bithiophene Rotamers. Table 2 lists the dipole moments and static (hyper)polarizabilities of the *anti-gauche* and *syn-gauche* 2,2'-bithiophene forms calculated at the HF/POL, MP2/POL, and BH&HLYP/POL levels. By analogy to the monomer, both the 2,2'-bithiophene forms exhibit a somewhat low polarity. Nevertheless, when passing from the *syn-gauche* to the *anti-gauche* conformer, the μ value decreases by ca. a factor of two, due to the mutual disposition of the monomeric thiophene rings. Note that, although the *syn-gauche* conformation reveals a rotated structure, its μ value is slightly less than $2 \times \mu$ (thiophene). On the other hand, in the case of the polarizabilities, the variations between

TABLE 2: Dipole moments (D), static electronic polarizabilities (a.u.), first-order hyperpolarizabilities (a.u.), and second-order hyperpolarizabilities (a.u.) of 2,2'-bithiophene rotamers^a.

	<i>anti-gauche</i>			<i>syn-gauche</i>		
	HF	MP2	BH and HLYP	HF	MP2	BH and HLYP
μ	0.52	0.31	0.40	1.21	0.72	0.93
α_{xx}	178.53	184.76	186.63	177.29	183.13	184.95
α_{yy}	84.85	86.72	84.30	125.80	127.96	126.58
α_{zz}	127.99	129.81	128.68	86.73	88.65	86.27
$\langle\alpha\rangle$	130.46	133.76	133.20	129.94	133.25	132.60
$\Delta\alpha$	81.71	85.28	89.22	78.70	82.29	85.98
β_{xxy}	2.7	-3.1	7.0	0.0	0.0	0.0
β_{yyy}	29.9	30.3	32.2	0.0	0.0	0.0
β_{zzy}	16.1	-3.3	7.0	0.0	0.0	0.0
β_{xxz}	0.0	0.0	0.0	45.7	31.5	59.0
β_{yyz}	0.0	0.0	0.0	22.5	-4.0	27.0
β_{zzz}	0.0	0.0	0.0	40.8	16.3	21.9
β_{μ}	48.7	23.9	46.2	109.0	43.8	107.9
γ_{xxxx}	102128			90352		
γ_{yyyy}	21824			22464		
γ_{zzzz}	21392			21216		
γ_{xxyy}	13312			12960		
γ_{xxzz}	6432			7744		
γ_{yyzz}	7536			6928		
$\langle\gamma\rangle^b$	39981			37859		

^aThe calculations were performed with the POL basis set on the MP2/6-311G** geometries.

^bThe HF/POL $\langle\gamma\rangle$ value of the thiophene monomer is calculated to be 14850 a.u..

the studied rotamers are significantly minor. In fact, the static MP2/POL $\langle\alpha\rangle$ value for the *syn-gauche* form is only 0.51 a.u. smaller than the corresponding value for the *anti-gauche* conformation (-0.4%). For both the dimers, α_{xx} is the largest component, recovering ca. 50% of the total polarizability ($\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$). The MP2/POL $\langle\alpha\rangle$ data overestimate the experimental datum obtained in tetrahydrofuran solution by ca. 10 a.u. (+7.7%) [59]; however, they are in good agreement with those previously computed at the MP2/aug-cc-pVDZ level for conformations in the 0-180° S-C₂-C₂'-S dihedral angle range [14]. Note that the present $\Delta\alpha$ values are slightly more influenced by the structure, increasing by ca. 3 a.u. (+3.6%) when passing from the *syn-gauche* to the *anti-gauche* rotamer. By analogy to the results found for the monomer, in comparison to the MP2/POL data, the HF/POL and BH&HLYP/POL methods furnish good $\langle\alpha\rangle$ and $\Delta\alpha$ estimates (within 2.5-4.4% and 0.4-4.6%, resp.). Similarly to the electronic polarizabilities, the $\langle\gamma\rangle$ values are little dependent on the conformation, decreasing by ca. 5% when going from the *anti-gauche* to the *syn-gauche* form. In addition, as for the calculated polarizabilities, the dominant γ component lies along the *x*-axis for both the *gauche* structures, amounting to ca. 50% of the total second-order hyperpolarizability ($\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz}$).

The dispersion effects (Table 3) evaluated at $\hbar\omega = 0.04282$ and 0.08564 a.u. increase the static $\langle\alpha\rangle$ ($\Delta\alpha$) values of both

TABLE 3: Static and frequency-dependent ($\hbar\omega = 0.04282$ a.u.) electronic polarizabilities (a.u.) and first-order hyperpolarizabilities (a.u.) of 2,2'-bithiophene rotamers^a.

	<i>anti-gauche</i>	<i>syn-gauche</i>
$\langle\alpha\rangle(0;0)$	130.46	129.94
$\langle\alpha\rangle(-\omega;\omega)$	132.57 (140.15)	131.97 (139.14)
$\Delta\alpha(0;0)$	81.71	78.70
$\Delta\alpha(-\omega;\omega)$	84.68 (96.33)	81.43 (92.48)
$\beta_{\mu}(0;0)$	48.7	109.0
$\beta_{\mu}(-\omega;\omega;0)$	51.3	116.1
$\beta_{\mu}(-2\omega;\omega;\omega)$	54.7	126.8

^aThe calculations were performed at the HF/POL level on the MP2/6-311G** geometries. The values in parentheses refer to the frequency-dependent polarizabilities at $\hbar\omega = 0.08564$ a.u..

the conformations, respectively, by ca. 2 and 7% (4 and 18%). It is of interest noting that the $\langle\alpha\rangle$ and $\langle\gamma\rangle$ data of the 2,2'-bithiophenes are greater than twice the corresponding values for the monomer, suggesting a some degree of interfering π -conjugation in the dimers.

Differently from the calculated polarizabilities and second-order hyperpolarizabilities, both the magnitude (Table 1) and direction (Figure 1) of the β_{μ} vector are noticeably affected by the structural features, almost following the behaviour found for the dipole moments.

In fact, for the *antigauche* form, the β_{μ} property which is aligned along the y -axis is predicted to be smaller than that for the *syn-gauche* rotamer (with β_{μ} aligned along the z -axis) by ca. a factor of two. This result is almost independent from the theoretical level and is observed for the static first-order hyperpolarizabilities as well as for the NLO SHG and EOPE processes. As for the monomer, the introduction of the MP2 electron correlation contributions is negative for β_{μ} , reducing the HF/POL data by 50–60%, the largest effect being found for the *syn-gauche* rotamer. Similar to the HF behavior, the BH&HLYP functional overestimates the MP2/POL β_{μ} values by 95–165%. It is of interest to note that, at the HF/POL level when passing from the monomer to the *syn-gauche* 2,2'-bithiophene, the static β_{μ} value increases by a factor of 2.6, although the dimer exhibits a nonplanar arrangement. Note that the corresponding monomer \rightarrow dimer increases obtained at the BH&HLYP/POL and MP2/POL levels are greater, being calculated to be 2.9 and 3.6, respectively.

Not surprisingly, for both the rotamers, $\beta_{\mu}(\text{SHG}) > \beta_{\mu}(\text{EOPE}) > \beta_{\mu}(\text{static})$ (Table 3). The dispersion effects estimated at $\hbar\omega = 0.04282$ a.u. increase the static β_{μ} values by 5–6% for the EOPE and 12–16% for the SHG NLO phenomenon, the largest percentages being predicted for the *syn-gauche* conformation.

4. Conclusions

The dipole moments and static and frequency-dependent electronic (hyper)polarizabilities of the *anti-gauche* and *syn-gauche* minimum-energy conformations of 2,2'-bithiophene were studied in the gas phase using *ab initio* HF, MP2, and DFT methods. The NLO properties for the SHG and EOPE phenomena were explored at $\lambda = 1064$ nm. The effects of electron correlation at MP2 level are remarkable especially for the first-order hyperpolarizabilities, reducing the HF data by 50–60%. The DFT methods, although furnishing good performance for the dipole moments and polarizabilities, significantly overestimate the MP2 first-order hyperpolarizabilities. The polarizabilities and second-order hyperpolarizabilities are little influenced by the conformation. By contrast, both the magnitude and direction of the dipole moment and first-order hyperpolarizabilities are strongly affected by the structural characteristics, the magnitudes increasing when going from the *anti-gauche* to the *syn-gauche* form by ca. a factor of two. On the basis of the present findings, the 2,2'-bithiophene rotamers might be identified through experimental SHG and EOPE NLO measurements.

Conflict of Interests

The author declares that there is no conflict of interests regarding the publication of this paper.

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