

Research Article

A Quantum Chemical Study on Structures and Electronic (Hyper)polarizabilities of 2,2'-Biselenophene Rotamers

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Geometries, IR and Raman spectra, nucleus independent chemical shifts, and static electronic (hyper)polarizabilities of the equilibrium conformations of 2,2'-biselenophene were determined in vacuum using density functional theory (DFT) computations. At the DFT-PBE0/6-31G+pd level the *antigauche* structure characterized by the Se-C₂-C_{2'}-Se dihedral angle of 157° is the global minimum, whereas the *syngauche* rotamer (Se-C₂-C_{2'}-Se = 40°) lies ca. 0.7 kcal·mol⁻¹ above the *antigauche* form. The structural and spectroscopic properties as well as the electronic polarizability of the *antigauche* are similar to those of the *syngauche* structure. On the other hand, the dipole moments and first-order hyperpolarizabilities are strongly influenced by the conformational characteristics, increasing by ca. a factor of five when passing from the *antigauche* to the *syngauche* form.

1. Introduction

Oligomers and polymers based on five-membered heterocycles have received great attention as promising conductive and nonlinear optical (NLO) materials [1–3]. Although the major efforts have been principally directed towards polyfurans, polypyrroles, and especially polythiophenes, recent studies have been also dedicated to the properties of polyselenophenes [4, 5]. Selenophene, owing to the intrinsic effects of the heavy atom, is considered an interesting building-block for the design of NLO devices [6–10]. Physicochemical properties of π -conjugated oligomers and polymers are usually influenced by the twisting degree of the backbone as well as by the extension of the electron delocalization [11, 12]. However, structural and electronic properties of large oligomers and polymers can be extrapolated by using data of smaller oligomers [11, 12].

Differently from the monomer, little is known about the physicochemical properties of the smallest oligoselenophenes. Structures and torsional potentials of 2,2'-biselenophene, 2,2':5',2''-terselenophene, and 2,2':5',2'':5'',2'''-quaterselenophene have been previously investigated by using *ab initio* and density functional theory (DFT) methods [13, 14]. On the basis of the most recent theoretical results

obtained in vacuum, 2,2'-biselenophene is predicted to exist in two nonplanar minimum-energy conformations, characterized by Se-C₂-C_{2'}-Se dihedral angles of ca. 150° (*antigauche*) and 40° (*syngauche*) [14]. The *antigauche* is the lowest-energy conformer, with the *syngauche* being predicted to lie above the *antigauche* structure by less than 1 kcal/mol [13, 14]. The torsional potentials of 2,2'-biselenophene for the 0°–360° rotation around the C₂–C_{2'} bond are described by flat four-well potentials, showing a high degree of conformational flexibility [13].

The present work reports important physicochemical properties of the most stable rotamers of 2,2'-biselenophene by using computational methods. The structures of the investigated conformations are displayed in Figure 1. Specifically, we determined the geometries, vibrational spectra, nucleus independent chemical shifts, dipole moments, and static electronic polarizabilities and first-order hyperpolarizabilities in the gas phase. To the best of our knowledge experimental and theoretical hyperpolarizabilities of 2,2'-biselenophenes are not available so far, whereas there are a number of studies available for the monomer selenophene [6–10]. Electronic first-order hyperpolarizabilities and the related NLO properties are often affected by conformational characteristics and could be helpful tools for isomeric identification [15–20].

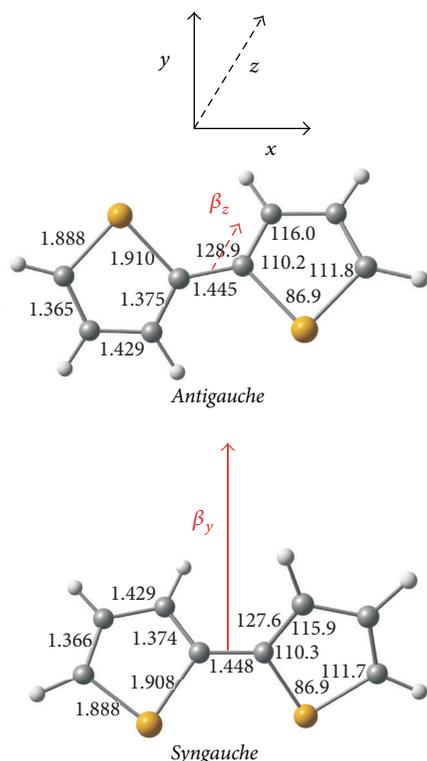


FIGURE 1: Equilibrium structures of 2,2'-biselenophene in gas. Bond lengths in Å, angles in degrees. $\beta_\mu(\text{syngauche}) = 263.5$ a.u., $\beta_\mu(\text{antigauche}) = 52.6$ a.u. Colors: white (hydrogen), grey (carbon), and yellow (selenium).

2. Computational Details

The calculations were performed using the GAUSSIAN 03 program [21]. The geometries of the *antigauche* and *syngauche* forms of 2,2'-selenophene (Figure 1) were optimized using the PBE0 DFT method [22], together with the basis set previously developed by Kamada et al. [23] for structural and (hyper)polarizability computations. It consists of 6-31G basis set for hydrogen atoms, 6-31G+pdd for carbon atoms ($\zeta_p = 0.0438$, $\zeta_{d1} = 0.18719$, and $\zeta_{d2} = 0.0438$), and LANLIDZ+pdd for selenium atoms ($\zeta_p = 0.0367$, $\zeta_{d1} = 0.11558$, and $\zeta_{d2} = 0.0367$), which also includes effective core-potential functions. This basis is here denoted as 6-31+pdd'. The vibrational analysis performed at the PBE0/6-31+pdd' level under the harmonic approximation shows that all the studied structures are equilibrium geometries (no imaginary frequencies). The static electronic polarizabilities (α) and first-order hyperpolarizabilities (β) were computed at the PBE0/6-31G+pdd' level through the coupled-perturbed HF (CP-HF) theory [24]. The following orientationally invariant quantities were employed:

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

$$\beta_\mu = \sum_{i=x,y,z} \frac{\beta_i \mu_i}{|\mu|}, \quad \beta_i = \frac{1}{3} \sum_{j=x,y,z} (\beta_{ijj} + \beta_{jij} + \beta_{jji}).$$
(1)

3. Results and Discussion

The *antigauche* form is the global minimum-energy structure, characterized by the Se-C₂-C₂'-Se dihedral angle of 157°. The *syngauche* form (Se-C₂-C₂'-Se = 40°) lies above the *antigauche* conformation by 0.68 kcal·mol⁻¹, in good agreement with previous *ab initio* and DFT results [13, 14], especially with the B3LYP/6-311++G** computations ($\Delta E = 0.73$ kcal·mol⁻¹) [14]. Thus on the basis of the present results, in the gas phase the *antigauche* is the prevailing structure (ca. 76%), with the *syngauche* being however an important conformation (ca. 24%). Note that, as can be appreciated from the data reported in Figure 1, the geometries of the *gauche* rotamers are very similar to each other. In particular, the bond lengths and angles of the *antigauche* differ, respectively, by no more than 0.003 Å (C₂'-C₂) and 1.3° (C₂'-C₂-C₃) from the corresponding values of the *syngauche* form. The structural similarity is also confirmed by the spectroscopic results. For both the rotamers we determined the nucleus independent chemical shift perpendicular to the plane of the selenophene ring at the distance of 1 Å [NICS(1)_⊥] [25, 26]. This parameter is closely connected to aromaticity, a negative NICS(1)_⊥ value denoting an aromatic ring [25, 26]. The PBE0/6-31+pdd' NICS(1)_⊥ values for the *antigauche* and *syngauche* 2,2'-biselenophenes are very close to each other, being calculated to be -17.6 and -17.3 ppm, respectively. Note that, when passing from the monomer to the dimer, the ring aromaticity decreases by ca. 20%.

The above results on the calculated geometries are also corroborated by the IR and Raman spectra obtained at the PBE0/6-31+pdd' level under the harmonic approximation. The simulated vibrational spectra in the 500–1800 cm⁻¹ range are displayed in Figure 2. The complete sets of wavenumber values (ω), IR intensities (I_{IR}), and Raman activities (A_{Raman}) of the *antigauche* and *syngauche* forms of 2,2'-biselenophene are given in Tables 1 and 2. The most active Raman peak of the *antigauche* form placed at 1526 cm⁻¹ ($A_{\text{Raman}} = 1594$ Å⁴/amu) is principally attributed to the C=C + C-C bonds stretching vibration with the nonnegligible contribution of in-plane C-H bending deformations (mode no. 9, Table 1). A graphical representation of the atom vector displacements involved in this mode is given in Figure 2(a). The corresponding transition for the *syngauche* conformation is blue-shifted by only 1 cm⁻¹ (Table 2). Additionally, the IR spectrum of both rotamers is dominated by an isolated band located at 673 cm⁻¹ for the *antigauche* ($I_{\text{IR}} = 126.5$ km/mol, mode no. 28) and at 682 cm⁻¹ for the *syngauche* ($I_{\text{IR}} = 118.4$ km/mol, mode no. 27). As can be seen in Figure 2(b), this transition is assigned to a pure out-of-plane bending deformation.

Beside to the structural and spectroscopic properties, now we explore the electric properties of the *gauche* rotamers. As a test case, we computed the electric properties also for the monomer, for which some experimental and high-level theoretical estimates are available from the literature. The experimental gas-phase dipole moment (μ) of selenophene at 0.39 D [27] is overestimated by the present calculations ($\mu = 0.47$ D), whereas the observed $\langle \alpha \rangle$ value of 74.90 a.u.

TABLE 1: Vibrational wavenumbers, ω (cm^{-1}), infrared intensities, I_{IR} (km/mol), and Raman activities, A_{Raman} ($\text{\AA}^4/\text{amu}$), of the *antigauche* form of 2,2'-biselenophene.

Mode no.	ω	I_{IR}	A_{Raman}
1	3280	0.0	378.7
2	3280	1.3	0.8
3	3227	0.2	322.4
4	3226	8.9	14.9
5	3206	17.7	5.4
6	3206	0.0	98.0
7	1631	0.2	940.4
8	1573	4.7	0.1
9	1526	1.2	1593.9
10	1515	29.4	1.3
11	1390	0.0	26.9
12	1352	4.0	0.4
13	1288	0.3	17.9
14	1241	27.9	0.6
15	1230	1.6	20.3
16	1110	1.1	0.5
17	1097	0.0	60.2
18	1072	0.4	29.2
19	1072	11.5	0.3
20	892	0.1	3.4
21	889	0.1	0.4
22	874	0.7	0.1
23	838	0.7	0.8
24	829	31.9	1.6
25	817	3.7	44.1
26	765	65.2	0.2
27	679	4.5	1.6
28	673	126.5	1.5
29	658	0.3	8.3
30	628	0.6	0.4
31	581	0.1	45.2
32	565	0.8	1.2
33	550	2.0	5.8
34	514	1.3	0.7
35	461	0.4	0.7
36	412	7.6	3.6
37	320	0.1	0.7
38	246	0.0	3.1
39	194	0.1	4.8
40	106	1.7	0.8
41	105	0.1	0.7
42	22	0.1	1.9

The calculations were carried out at the PBE0/6-31 + pdd' level.

[28] is reasonably reproduced by the PBE0/6-31+pdd' level ($\langle\alpha\rangle = 70.44$ a.u., -6%). Unfortunately, the experimental first-order hyperpolarizability of selenophene is not available to date. However, the PBE0/6-31G+pdd' β_{μ} value of selenophene of 98.2 a.u. is in excellent agreement with the datum

TABLE 2: Vibrational wavenumbers, ω (cm^{-1}), infrared intensities, I_{IR} (km/mol), and Raman activities, A_{Raman} ($\text{\AA}^4/\text{amu}$), of the *syngauche* form of 2,2'-biselenophene.

Mode no.	ω	I_{IR}	A_{Raman}
1	3279	1.0	367.3
2	3279	0.1	13.3
3	3229	6.6	238.9
4	3228	3.0	103.6
5	3212	0.0	59.3
6	3211	13.2	103.0
7	1624	0.6	755.4
8	1574	0.2	4.3
9	1527	14.9	1151.6
10	1507	6.3	15.4
11	1377	1.3	39.0
12	1373	1.0	9.9
13	1285	4.4	21.9
14	1263	45.0	8.1
15	1199	14.3	1.1
16	1109	0.2	4.6
17	1096	0.1	30.5
18	1070	2.0	0.4
19	1057	13.0	20.2
20	895	1.1	0.4
21	893	0.0	5.4
22	890	1.8	1.6
23	847	3.1	14.8
24	835	28.5	0.1
25	821	14.8	33.7
26	784	30.0	1.4
27	682	118.4	0.4
28	680	11.0	2.4
29	658	2.5	3.5
30	651	4.8	5.9
31	573	0.9	8.5
32	554	1.8	0.5
33	520	3.1	7.6
34	504	1.3	7.8
35	476	0.0	24.3
36	423	7.4	0.3
37	287	0.1	1.2
38	257	0.5	1.9
39	245	0.0	6.4
40	102	1.6	1.2
41	80	0.1	1.7
42	37	0.0	5.3

The calculations were carried out at the PBE0/6-31 + pdd' level.

previously predicted by the CCSD(T)/6-31G+pdd' computations at 98.4 a.u. (with a deviation of -0.2%) [7].

Similarly to the monomer, both 2,2'-biselenophenes show a rather low polarity. However, due to the mutual arrangement of the selenophene moieties, when going from

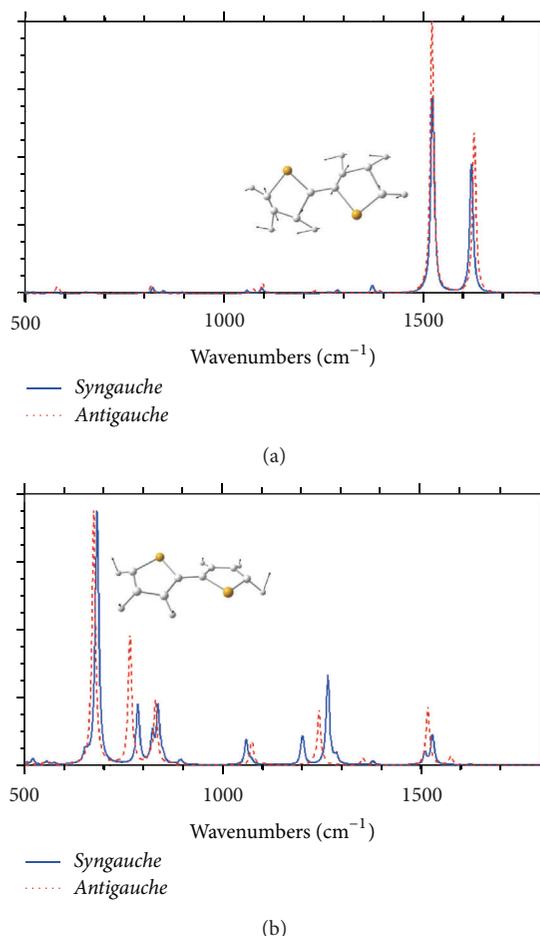


FIGURE 2: Simulated gas-phase Raman (a) and IR (b) spectra of 2,2'-biselenophene *antigauche* and *syngauche* conformations. Lorentz line shapes with half-width of 10 cm^{-1} are used. PBE0/6-31+pdd' results.

the *antigauche* to the *syngauche* form, the μ value increases by ca. a factor of five ($\mu = 0.19\text{ D}$ versus $\mu = 0.88\text{ D}$). A somewhat different behaviour occurs for the electronic polarizabilities, with the $\langle\alpha\rangle$ (*syngauche*) value of 150.76 a.u. being very close to the corresponding datum of the *antigauche* structure (152.74 a.u. , +1%). By contrast, both the magnitude and direction of the β_{μ} vector (see Figure 1) are strongly influenced by the conformation, in line with the results obtained for the dipole moments. Specifically, the β_{μ} vector for the *antigauche* form is directed along the z -axis, whereas for the *syngauche* rotamer it is aligned along the y -axis. More importantly, the present PB0/6-31G+pdd' calculations predict $\beta_{\mu}(\textit{syngauche}) > \beta_{\mu}(\textit{antigauche})$ by ca. a factor of five.

4. Conclusions

The present results indicate that the calculated electronic polarizability and structural and spectroscopic properties of 2,2'-biselenophenes are little dependent on the conformation. Differently, both the magnitude and direction of the dipole moment and first-order hyperpolarizability are significantly

influenced by the structural features. Therefore the *gauche* rotamers could be unambiguously discriminated on the basis of their rather different NLO signals.

Conflict of Interests

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

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