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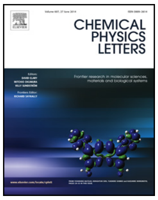

Second-order nonlinear optical responses of heptahelicene and heptathiahelicene derivatives

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ABSTRACT

Using quantum chemistry methods, structure–NLO property relationships are investigated for families of 7-ring helicenes built from thiophene and benzene rings. In absence of donor or acceptor substituents, the first hyperpolarizability (β) is small. On the other hand, with NO_2 groups in terminal positions β increases, especially for helicenes containing few benzene rings. For NMe_2 substituents the enhancement is damped by the less polarizable benzene rings, the cross-conjugated all-thiophene segments, and the auxiliary acceptor character of the thiophenes. From this analysis, we selected three helicenes and conjectured larger β upon replacing the thiophenes by furans. This hypothesis has been verified.

1. Introduction

Large first hyperpolarizability (β) results from the balance between delocalization and asymmetry. This has been demonstrated for several classes of compounds. In push–pull π-conjugated systems, (i) for a given pair of D/A substituents, β increases with the electron delocalization – often related to the bond length alternation – until a maximum is attained and then it decreases while (ii) for a given π-conjugated linker, β increases also with the strength of the D/A pair until a maximum is reached [1]. Another class of compounds that can exhibit large β values are $(AB)_n$ chains, like polymethineimine. In that case, the first hyperpolarizability is zero when the bond length alternation vanishes or when the A and B sites get similar [2]. This interplay between the asymmetry, the delocalization, and the first hyperpolarizability is also modulated by the molecular shape. Among shaped systems, helical systems belong to a specific category of which the properties depend on their length and on their pitch, also displaying dynamical behavior as a function of the temperature, of the solvent, and of the presence of electrolytes [3–5]. This Letter addresses the first hyperpolarizability of some of their representatives, helicenes [6–10].

Helicenes are fascinating π-conjugated compounds in which a regular helix is formed through the all-*ortho* fusion of aromatic rings as a result of steric repulsions between the rings and/or their substituents. Such structures present a large potential to display remarkable electronic, optical, and magnetic properties due to their chiral π-electron network and the related chiro-optical signatures. Recent and less recent literature presents numerous investigations on the synthesis [11–21], on the structure determination, on the characterization of the electronic, redox, optical, and chiro-optical properties [22–30] of homo- and hetero-helicenes as well as of their substituted derivatives. Their nonlinear optical (NLO) properties have also been of interest, owing to the possibility of combining π-conjugation and asymmetry [31–36]. So, several investigations have addressed the design of helicenes presenting large second-order NLO responses, via substitution of the conjugated helical backbone by appropriate donor and/or acceptor groups [34]. Helicenes were also described as appropriate candidates for exhibiting two-photon circular dichroism (TP-CD) phenomenon [35,36].

Several thiahelicenes have been synthesized over the last decades, demonstrating specific properties [7–11,13,28]. So, some of our recent contributions have considered tetrathia[7]helicene, where the thiophene and benzene rings alternate along the helix, constituting the midpoint between heptahelicene and heptathiahelicene [34]. More recently, several works [37,38] have reported the synthesis of thiahelicenes – also called carbon–sulfur helicenes or $(C_2S)_n$ helicenes – with different content in phenyl rings, controlling therefore the delocalization along the helix. In this Letter, we consider the whole range of benzene/thiophene variations in symmetric seven-ring helicenes (Figure 1) and we addressed their first hyperpolarizabilities by using *ab initio* calculations. First, β is calculated for the non-substituted helicenes to highlight the

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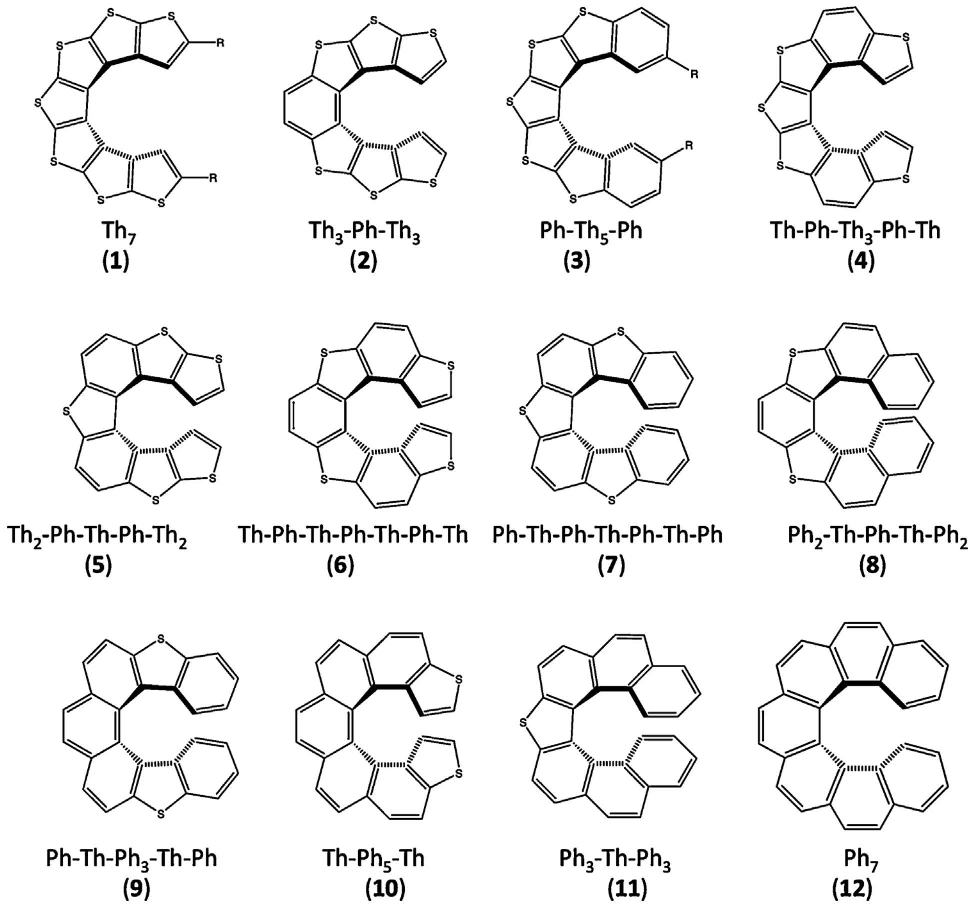

Figure 1. Derivatives of hepta- and heptathiahelicenes. R = H, NO_2, or NMe_2. Their position is illustrated for compounds **1** and **3**.

intrinsic second-order NLO response of the backbone. In a second step, we characterize their substituted analogs, obtained when a pair of nitro acceptor groups or a pair of dimethylamino donor groups is placed at the helicene extremities. *A priori*, it is difficult to predict which backbone(s) will provide the largest β responses. Indeed, owing to their cross-conjugated π-systems all-thiophene helicenes present the smallest electron delocalization. This is reflected in the wavelength of maximum absorption, which increases in the order **1** < **2** < **7** [37]. On the other hand, it is known that D/A substituted oligothiophenes display larger β values than their corresponding oligophenylenes [39]. Our computational investigation aims therefore at assessing which of these competing effects is the strongest. Section 2 of this Letter describes the computational approaches. The results are presented and discussed in Section 3 before conclusions are drawn in Section 4.

2. Theoretical and computational method

The helicene geometries were optimized at the density functional theory (DFT) level of approximation using the B3LYP hybrid exchange-correlation functional and the 6-311G(d) basis set. The Time-Dependent-Hartree–Fock (TDHF) scheme [40] was applied for obtaining the dynamic first hyperpolarizabilities, considering an incident wavelength of 1064 nm. In addition frequency-dependent hyperpolarizability calculations were also performed using a long-range corrected exchange-correlation (XC) functional, LC-BLYP with a range-separating parameter μ of 0.47. Although its advantages with respect to the TDHF method remain an open question [39,41], long-range corrected XC functionals have been shown to correct conventional DFT schemes for their shortsightedness drawbacks [39,42–45]. The 6-311+G(d) basis set was employed in all the β calculations.

Though for second-harmonic generation (SHG) process, the β tensor contains 18 independent elements, experiment probes only different combinations of these [46], (i) the hyper-Rayleigh scattering (HRS) response, $\beta_{HRS}(-2\omega;\omega,\omega)$, and (ii) $\beta_{//}(-2\omega;\omega,\omega)$, the quantity, which can be deduced from electric field-induced second harmonic generation (EFISHG) measurements. $\beta_{HRS}(-2\omega;\omega,\omega)$ is here related to the HRS intensity for non-polarized incident light and observation of plane-polarized scattered light made perpendicularly to the propagation plane. It reads

$$\beta_{HRS}(-2\omega;\omega,\omega) = \sqrt{\left\{\left\langle\beta^2_{ZZZ}\right\rangle + \left\langle\beta^2_{ZXX}\right\rangle\right\}} \qquad (1)$$

The corresponding depolarization ratio (DR)

$$\mathrm{DR} = \frac{I^{2\omega}_{VV}}{I^{2\omega}_{HV}} = \frac{\left\langle\beta^2_{ZZZ}\right\rangle}{\left\langle\beta^2_{ZXX}\right\rangle} \qquad (2)$$

has values determined by the shape of the NLO-phore. $\left\langle\beta^2_{ZZZ}\right\rangle$ and $\left\langle\beta^2_{ZXX}\right\rangle$ are orientational averages of the β tensor that are calculated without assuming Kleinman's conditions. They correspond to measurements performed in the VV (vertically polarized incident and scattered lights) and HV (horizontally polarized incident light and vertically polarized scattered light) configurations, respectively. On the other hand, $\beta_{//}(-2\omega;\omega,\omega)$ corresponds to the projection of the