



# Quantum chemistry study on the third-order nonlinear optical properties of spirobifluorene derivatives



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## ABSTRACT

We investigate the electronic properties and dynamic second hyperpolarizabilities of spirobifluorene derivatives by using quantum chemistry calculations. We find that studied spirobifluorene derivatives exhibit both large second hyperpolarizability and excellent transparency. In addition, the second hyperpolarizabilities  $\langle\gamma(-2\omega; \omega, \omega, 0)\rangle$  and  $\langle\gamma(-\omega; \omega, 0, 0)\rangle$  increase with raising the frequency of incident light, and the increasing extent of  $\langle\gamma(-2\omega; \omega, \omega, 0)\rangle$  is larger than that of  $\langle\gamma(-\omega; \omega, 0, 0)\rangle$ . Resonance enhancement observed results in a significant dispersion of the  $\langle\gamma\rangle$  values in visible region. The effects of the basis sets and substituent group on the polarizability and second hyperpolarizability are also discussed respectively.

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## 1. Introduction

Organic nonlinear optical (NLO) materials have attracted keen attention in recent years because of their potential applications in photonic technologies such as optical communications, computing and data storage, and image processing [1–3]. Most investigated chromophores for NLO applications are donor (D)–acceptor (A) substituted  $\pi$ -conjugated organic molecules. The increase in NLO response of such chromophores is usually accompanied by bathochromic shifts of the maximum absorption peak, which can decrease the optical transparency of the NLO chromophores [4]. Therefore, most NLO chromophores synthesized for electro-optic and second harmonic generation application typically exhibit trade-off between nonlinearities and transparency [5].

Recently, special attention has been paid to spiroconjugated molecular systems because spirocompounds have exceptionally larger NLO properties compared to the corresponding monomers although the respective lowest-energy electronic transition wavelength shows rather small shift [6–11]. The enhancement of first hyperpolarizability of spirocompounds has been explained based on the orbital interaction through the spiro linkage [7], that is, spiroconjugation effect [8]. As a typical spirocompound, spirobifluorene has excellent third-order NLO properties [10]. Most of the earlier investigations of the NLO response of the spirobifluorene derivatives considered the first hyperpolarizability [8], however,

few theoretical work have been done to study the second hyperpolarizability of such molecular species.

Quantum chemistry is closely involved in the understanding of the physical phenomena of NLO responses of molecules because of its ability to predict the structure–properties relationship. In this study, we use quantum chemistry calculations to study the electronic properties and (dynamic) second hyperpolarizability of spirobifluorene derivatives (Fig. 1). Our results demonstrate that the studied spirobifluorene derivatives exhibit both high transparency and large second hyperpolarizability, and thus become promising candidates for third-order NLO materials.

## 2. Theory and computational methods

In nonlinear optics, the polarization of a compound induced by an external radiation field is often approximated as a creation of an induced dipole moment by an external electric field. The energy ( $U$ ) of a molecule in presence of a static homogeneous electric field  $E$  can be expanded as follows:

$$U(E) = U(0) - \sum_i \mu_i E_i - \frac{1}{2!} \sum_{ij} \alpha_{ij} E_i E_j - \frac{1}{3!} \sum_{ijk} \beta_{ijk} E_i E_j E_k - \frac{1}{4!} \sum_{ijkl} \gamma_{ijkl} E_i E_j E_k E_l - \dots \quad (1)$$

where the subscripts  $i, j, k$ , and  $l$  represent  $x, y$  or  $z$  of Cartesian coordinate system,  $U(0)$  is the energy of the compound in the absence of  $E$ ,  $\mu_i$  is the molecular permanent electric dipole moment along the

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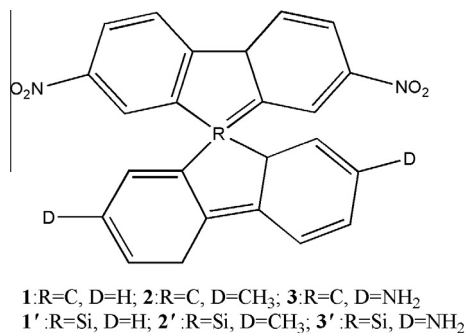


Fig. 1. The typical structures of spirobifluorene derivatives.

ith direction,  $E_i$  is the  $i$ th component of  $\vec{E}$ .  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are the linear polarizability, the first hyperpolarizability and second hyperpolarizability tensors, respectively. In dynamic electric fields,  $\alpha_{ij}$ ,  $\beta_{ijk}$  and  $\gamma_{ijkl}$  are frequency-dependent and related to different optical responses [12]. For third-order NLO responses, the static, dc-Kerr (EOKE), electric field-induced second harmonic generation (EFISHG), third harmonic generation (THG), and degenerate four-wave mixing (DFWM) responses are then given by  $\gamma(0;0,0,0)$ ,  $\gamma(-\omega; \omega, 0, 0)$ ,  $\gamma(-2\omega; \omega, \omega, 0)$ ,  $\gamma(-3\omega; \omega, \omega, \omega)$ , and  $\gamma(-\omega; \omega, -\omega, \omega)$ , respectively. In this study, the average linear polarizability  $\langle\alpha\rangle$  and second hyperpolarizability  $\langle\gamma\rangle$  values have been calculated using the following expressions, respectively [7]:

$$\langle\alpha\rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (2)$$

$$\langle\gamma\rangle = [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]/5 \quad (3)$$

The structures of the chosen compounds were fully optimized using the density functional theory (DFT) B3LYP method with a 6-31+G(d,p) basis set. Vibrational frequencies were calculated to confirm the equilibrium geometries that correspond to energy minima. After that, the static and frequency-dependent polarizability and hyperpolarizability tensor elements were calculated using the finite field (FF) scheme [12]. Finally, the electronic spectra were calculated by the time-dependent (TD) B3LYP/6-31+G(d,p) method. All calculations were carried out using the Gaussian 09 program [13].

### 3. Results and discussion

In our previous work [14], we found that both the electron correlation effect and the quality of the basis set are important for the hyperpolarizability calculations. In order to estimate the basis set dependence of  $\alpha$  and  $\gamma$ , we used the five Pople basis sets (e.g., 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p) and 6-311++G(d,p)) to calculate the average static polarizability  $\langle\alpha(0;0)\rangle$  and average static second hyperpolarizability  $\langle\gamma(0;0,0,0)\rangle$  of molecule 1, at levels of theory of HF, B3LYP, CAM-B3LYP and BHandHLYP, respectively. The calculated results were displayed in Figs. 2 and 3, respectively.

As expected, the considered basis sets have important impact on  $\langle\gamma(0;0,0,0)\rangle$  values for both DFT and HF approaches. Obviously, 6-31G(d,p)  $\equiv [1s1sp1sp1d/2s1p]$  for heavy atom/hydrogen atoms respectively, is not exactly suitable for hyperpolarizability calculations because it is TIGHT. Addition of one set of diffuse functions (i.e., 6-31+G(d,p)) significantly improves the results. So diffuse functions are important to obtain accurate results for the hyperpolarizability [15,16]. However, when going from 6-31+G(d,p) to 6-31++G(d,p) and to 6-311++G(d,p), the value of  $\langle\gamma(0;0,0,0)\rangle$  maintains nearly unchanged. Similar conclusions can be also drawn in the case of  $\langle\alpha(0;0)\rangle$ . It should be noted that calculations of the hyperpolarizability are typically difficult to converge with basis

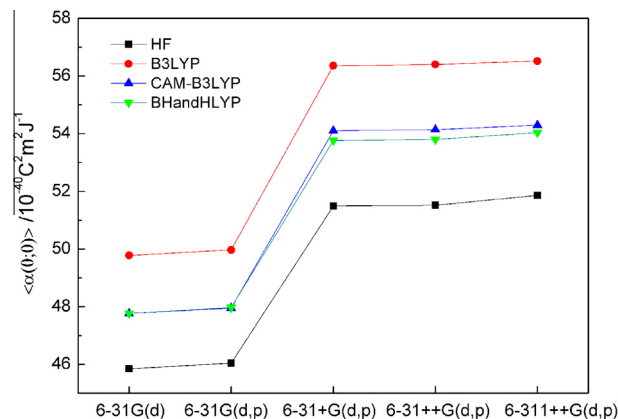


Fig. 2. The basis set effect of  $\langle\alpha(0;0)\rangle$  of molecule 1 calculated at various levels of theory.

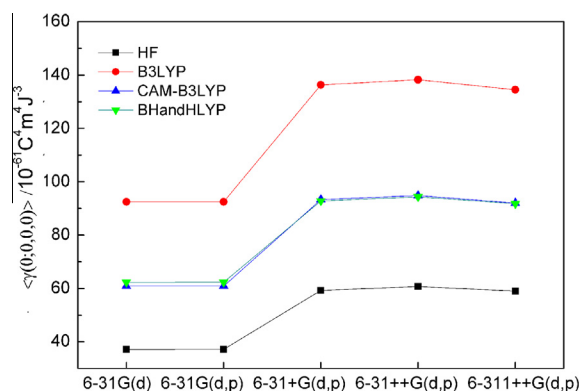


Fig. 3. The basis set effect of  $\langle\gamma(0;0,0,0)\rangle$  of molecule 1 calculated at various levels of theory.

set size. In order to understand these convergence issues and thus obtain accurate ab initio values, one should compare calculations of the static hyperpolarizability using different kinds of basis sets (see Refs. [16–18] for detail). Here we select the 6-31+G(d,p) basis set to calculate the static and dynamic second hyperpolarizabilities in order to reduce the computational cost. Moreover, the  $\langle\gamma(0;0,0,0)\rangle$  value also changes at different levels of theory. We found that  $\langle\gamma\rangle_{\text{B3LYP}} > \langle\gamma\rangle_{\text{CAM-B3LYP}} \approx \langle\gamma\rangle_{\text{BHandHLYP}} > \langle\gamma\rangle_{\text{HF}}$  for the same basis set. Here we select CAM-B3LYP method to calculate the static and dynamic second hyperpolarizabilities of spirobifluorene systems in this study.

We also calculated the electronic spectra, frontier molecular orbitals energy gap, dipole moment,  $\langle\alpha(0;0)\rangle$  and  $\langle\gamma(0;0,0,0)\rangle$  of studied spirobifluorene systems (i.e., molecules 1–3 and 1'–3'), which were listed in Table 1. For molecule 1–3, the maximum absorption wavelengths calculated here are in a good agreement with ZINDO results [8]. From the Table 1, we can also observe that studied spirobifluorenes systems all present a good non-absorbance band in the visible range for expected applications. Other noticeable characteristic in the absorption spectrum is a wide transparency window within the range of 415 nm which is desirable for NLO crystals because the absorptions in an NLO material near the fundamental or second harmonic signals will lead to the loss of the conversion of SHG. In addition, spirobifluorene systems also exhibit large second hyperpolarizability due to the spiroconjugation effect. For molecules 1–3 as well as molecules 1'–3', when substituent group D (in Fig. 1) changes from –H to –CH<sub>3</sub> and to –NH<sub>2</sub>, the ability of electron donor to donate electrons is enhanced, resulting in the decrease of frontier molecular orbitals energy gap

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