



Second-order nonlinear optical responses of carboranyl-substituted indole/indoline derivatives: impact of different substituents



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ABSTRACT

Carborane has been the subject of great interest over the last decades due to its high structural, chemical, biological stability and diverse applications. In the present work, carboranyl-substituted indole/indoline compounds and their functionalized derivatives have been systematically investigated by density functional theory (DFT) method with the view of assessing their electronic structures and first hyperpolarizabilities. Significantly, the first hyperpolarizabilities can be obviously enhanced by the introduction of a strong electron-withdrawing group for closed-ring forms, while the strong electron-donating group is beneficial for large first hyperpolarizabilities for open-ring forms. It indicates that the NLO properties of these compounds can be enhanced by controlling their relative substituent groups. Furthermore, the time-dependent DFT calculation illustrates that the enhancement of the first hyperpolarizabilities are found due to the obvious charge transfer (CT) transition, and closed-ring forms have a significant difference on the CT patterns versus open-ring ones. Investigation of the structure–property relationship and substituent effects at the molecular level can benefit for further exploration of carboranyl-substituted indole/indoline derivatives with versatile and fascinating NLO properties.

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1. Introduction

During the past several decades, nonlinear optical (NLO) processes are being theoretically and experimentally explored in a variety of optoelectronic modulators for optical telecommunication and photonic applications [1–6]. Great efforts have been devoted to designing and synthesizing high-performance NLO materials for their potential applications in low-cost, highly-efficient photonic and electro-optical devices [5,7–14]. It is crucial to study the various NLO chromophores and their properties for designing and synthesizing new NLO materials. To date, many strategies have been proposed to enhance the NLO responses, including increasing the strength of the donor/acceptor groups [15], twisting p-electron systems [16–18], expanding the length of the π -conjugated bridge [9,15,19,20], introducing a transition metal atom into the organic compounds [15,21,22] and so forth.

The quasi-icosahedral dicarba-closo-dodecarboranes isomers 1,2-(ortho-), 1,7-(meta-) and 1,12-(para-) $C_2B_{10}H_{12}$ are the best-known carboranes and have long been investigated for their high structural, chemical, biological stability and diverse applications

[23,24], including as DNA-binding boron sources for boron neutron capture therapy (BNCT) [25] and their potential use as a component of NLO materials [26–28]. In addition, it has been reported that the addition of donor and acceptor groups to the parent polyhedral borane and carborane can significantly increase the molecular dipole moments of the substituted species, which strongly contributes to the very large observed NLO response [29,30]. Up to now, carborane compounds as the smart optical luminescence and NLO materials have been widely investigated [27,31,32]. For example, a novel class of two-dimensional Λ - and W-shaped sandwich metallocarborane-containing chromophores have been founded and switchable NLO response induced by rotation of metallocarboranes $[Ni^{III/IV}(C_2B_9H_{11})_2]^{-/0}$ and C-, B- functionalized derivatives were studied by our group [33,34].

Recently Zhao et al. reported a new methodology, which provides an efficient, chemoselective, and highly controllable synthesis of carboranyl-substituted indoles and indolines [35]. Considering the unique properties of indoles and carboranes, carborane functionalized indoles or indolines may find applications in medicine and materials. Thus, it is important to carry out theoretical studies aiming to understand molecular aspects of such compounds and derivatives. However, a detailed understanding of carboranyl-substituted indoles and indolines for the optimization of the first hyperpolarizability is still lacking. In this paper, we took **1c** and **1o**

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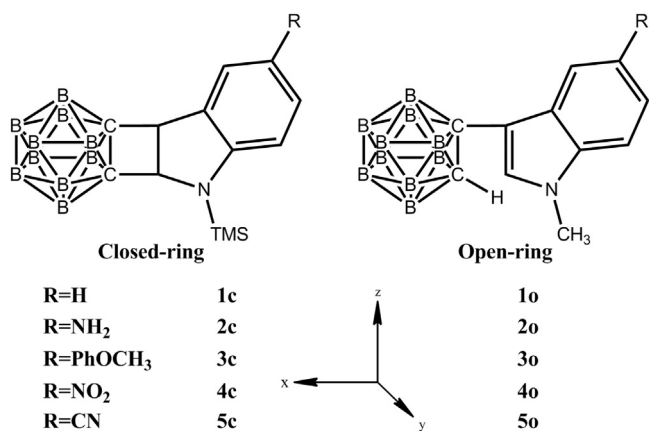


Fig. 1. Calculation models of closed-ring compounds **1c–5c**, and open-ring compounds **1o–5o**.

(**c** stands for the closed-ring form, while **o** represents the opening form) as the object of study, and replaced amino (–NH₂), methoxyphenyl (–C₆H₄–OCH₃), nitryl (–NO₂), cyano (–CN) with –H on the benzene ring of indole to form a range of *o*-carborane derivatives (Fig. 1). The purpose of the present work is to systematically study the substituent effects on the structures, NLO properties and electron spectra of carboranyl-substituted indole/indoline compounds and their functionalized derivatives by density functional theory (DFT) method, and provide a theoretical guidance for searching new NLO materials.

2. Computational details

The ground state geometries of all studied compounds were optimized by PBE1PBE, M06-2X and CAM-B3LYP functionals at the 6-31G* basis set with no symmetry constraint. And frequency calculations were carried out to identify each stationary point as a minimum. Based on the optimized geometries, natural bond orbital (NBO) population analysis was performed at the PBE1PBE/6-31+G* level.

The response of a molecule to a homogeneous static electric field can be represented by the following Taylor expansions [36]:

$$E^0 - \mu_i^0 F_i - \left(\frac{1}{2!}\right) \alpha_{ij} F_i F_j - \left(\frac{1}{3!}\right) \beta_{ijk} F_i F_j F_k - \left(\frac{1}{4!}\right) \gamma_{ijkl} F_i F_j F_k F_l - \dots \quad (1)$$

In this expression, E^0 is the energy of the molecule in the absence of an electric field, μ_i^0 is the permanent dipole moment, α_{ij} is the polarizability, and β_{ijk} and γ_{ijkl} are the first and second hyperpolarizabilities, respectively. The subscripts *i*, *j*, and *k* label the *x*, *y*, and *z* components, respectively. It is clear that the values of μ_i^0 , α_{ij} , β_{ijk} and γ_{ijkl} can be obtained by differentiating E with respect to F .

The total static first hyperpolarizability β_{tot} was calculated using the following equation:

$$\beta_{tot} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2} \quad (2)$$

the individual static component β_i was defined as:

$$\beta_i = \beta_{iii} + \frac{1}{3} \sum_{i \neq j} [(\beta_{ijj} + \beta_{jij} + \beta_{jji})] \quad i, j = x, y, z \quad (3)$$

β_{vec} , the projection of first hyperpolarizability on dipole moment vector μ , is related to electric field induced second harmonic generation (EFISH). This quantity usually is written as:

$$\beta_{vec} = \sum_i \mu_i \beta_i / |\mu| \quad i, j = x, y, z \quad (4)$$

To compute the first hyperpolarizability, one option is to take the derivatives either numerically or analytically. Numerically derivatives, also known as finite field (FF) calculations, can be achieved by using polynomial fits of either energy or induced dipole moment as a function of field strength. The nonlinear expansion coefficients from these fits correspond to the microscopic nonlinear optical property. The numerically derivatives used finite difference method provides a straight forward computational technique applicable to almost any quantum chemical formalism. When the molecule is considered to be in a uniform electric field F_i , in this case the energy expression reduces to:

$$E(F_i) = E^0 - \mu_i F_i - \left(\frac{1}{2!}\right) \alpha_{ii} F_i^2 - \left(\frac{1}{3!}\right) \beta_{iii} F_i^3 - \left(\frac{1}{4!}\right) \gamma_{iiii} F_i^4 - \dots \quad (5)$$

When the molecule is considered to be in two electric fields F_i and F_j , in this case the energy expression reduces to:

$$E(F_i, F_j) = E^0 - \mu_i F_i - \mu_j F_j - \left(\frac{1}{2}\right) \alpha_{ii} F_i^2 - \left(\frac{1}{2}\right) \alpha_{jj} F_j^2 - \alpha_{ij} F_i F_j - \left(\frac{1}{6}\right) \beta_{iii} F_i^3 - \left(\frac{1}{2}\right) \beta_{ijj} F_i^2 F_j - \left(\frac{1}{2}\right) \beta_{jji} F_j^2 F_i - \left(\frac{1}{6}\right) \beta_{jjj} F_j^3 - \left(\frac{1}{24}\right) \gamma_{iiii} F_i^4 - \left(\frac{1}{4}\right) \gamma_{ijjj} F_i^2 F_j^2 - \left(\frac{1}{6}\right) \gamma_{ijji} F_i F_j^3 - \left(\frac{1}{6}\right) \gamma_{jiji} F_j^3 F_i - \left(\frac{1}{24}\right) \gamma_{jjjj} F_j^4 - \dots \quad (6)$$

By truncating Eq. (5) after the F^4 term, and evaluating the energy at field strengths $\pm F_i$, $\pm 2F_i$, (F_i, F_j) , $(F_i, -F_j)$, $(-F_i, F_j)$, $(-F_i, -F_j)$ for Eqs. (5) and (6), the values of corresponding α , β and γ can be obtained respectively [37]. However, this method is very time-consuming, because it needs to calculate many times single point calculation under different values and directions of the external electric field. Moreover, the high-order derivative values would be inaccurate due to the accumulation of numerical differencing errors, which lead to the hyperpolarizabilities can not compare with actual values as well.

The analytical derivatives is also called coupled-perturbation Hartree-Fock (CPHF) methods, pioneered by Gerratt and Mills [38], Pulay [39], Pople et al. [40], and others [41–43]. The CPHF procedure may be generalized to higher order. Extending the expansion to high order allows the derivation of an equation for the high-order change in the MO coefficients, by solving a high-order CPHF equation. For basis set dependent perturbations, the first-order CPHF

equations are only needed for calculating high order derivatives, which have terms involving high order derivatives of the integrals themselves. Before the first-order CPHF equations, we should know a Hartree-Fock (HF) equation. The HF equation in the atomic orbital basis is written as:

$$F_i \sum_{\alpha} c_{ai} \chi_{\alpha} = \varepsilon_i \sum_{\alpha} c_{ai} \chi_{\alpha} \quad (7)$$

Each MO is expanded in terms of the basis functions χ , conventionally called atomic orbitals (MO=LCAO, Linear Combination of Atomic Orbitals). All the M_{basis} equations may be collected in a matrix notation.

$$FC = SC\varepsilon \quad (8)$$

The F matrix contains the Fock matrix elements, while the S matrix contains the overlap elements between basis functions. C is the matrix of coefficients of the atomic orbitals making up the molecular orbitals. ε is the orbital energy matrix and the condition that it be block-diagonal serves to determine the orbital set. An equation

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