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Quantum chemical study of structures, electronic spectrum, and nonlinear optical properties of polynuclear lithium compounds

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ABSTRACT

A theoretical study of polynuclear lithium compounds has shown that these species display large calculated nonlinear optical (NLO) responses. These compounds are based on aromatic subunits connected through polyhedral inorganic core (Li_7O_6 or Li_8O_6). These compounds show the calculated first hyperpolarizabilities (β) ranging from 262.55 to 16336.35 $\times 10^{-33}$ esu. The results show that subtle structural modification can substantially enhance the first hyperpolarizability. A basis for understanding the origin of these large NLO responses is proposed based on consideration of the molecular orbitals and electronic transition features of the compounds and the two-state model. Charge transfer from central core to the peripheral phenyl groups plays a key role in the nonlinear optical response. Moreover, the effects of different functionals and basis sets on first hyperpolarizability were systemically investigated.

1. Introduction

The design of novel materials with large nonlinear optical (NLO) responses is currently of great interest due to their potential applications in optical and electro-optical devices. There are three generic classes of nonlinear optical (NLO) materials: inorganic salts, semiconductors, and organic compounds. Each class possesses its own complement of favorable and unfavorable attributes for NLO application [1]. Although inorganic salts have a large transparency range, are robust, are available as large single crystals, the purely electronic NLO effects are often accompanied by those arising from lattice distortions; response times are slow; and synchronization of the phase of the interacting optical fields is not easy to satisfy [2]. NLO response of semiconductors originates from saturable absorption. Their third-order NLO responses are among the largest known [3], but the NLO processes based on such resonant interactions may be relatively slow. The organic materials exhibit relatively low cost, ease of fabrication and integration into devices, tailorability, which allows one to fine-tune the chemical structure and properties for a given nonlinear optical process, high laser damage thresholds, low dielectric constants, fast nonlinear optical response times, and off-resonance nonlinear optical susceptibilities comparable to or exceeding those of ferroelectric inorganic crystals [4]. The main disadvantages of organic materials are low thermal stability, a facile relaxation to random orientation in poled guest–host systems, low optical transparency in the UV–vis region result from low-energy transitions [5]. The limitations identified above spur investigations of novel NLO materials. Recent study shows that organometallic complexes offer greater scope for creation of multifunctional NLO materials by virtue of their greater design flexibility and low energy, yet sometimes intense electronic transitions [6–10].

Lithium has the lightest weight among metallic elements, and a very rich chemistry [11]. Organolithium compounds thus constitute an important and active field of studies with numerous applications [12,13]. Here, we mainly focused on their NLO properties. $LiNbO_3$ has exhibited excellent NLO response and is widely applied as inorganic NLO material [14,15]. Lithium 3,5-dinitrobenzoate (Li(dnb)) was synthesized and charactered, which can form a 1D propeller chain structure and exhibits modest second-order nonlinear response [16]. Zhao et al. investigated the structural, electronic, and optical properties of medium-sized Li_n clusters (n = 20, 30, 40, 50) and found that the average polarizability of the Li clusters reduces rapidly with cluster size and can be approximately described by a classical metallic sphere model [17]. Li et al. theoretically designed and investigated NLO properties of series of Li-doped electrode/salt complexes. These alkali–metal-doped complexes have shown a remarkably large NLO response, and the Li valence electron played a crucial role in the large NLO value of these compounds [18–22]. Our group also investigated the NLO properties of the lithium decahydroborate (Li@B10H14) complex [23]. However, there are no NLO experimental reports on these Li-doped electrode/salt complexes, which might be due to the instability of these complexants and/or inadequate reactivity of the Li atom caused by the presence of some repulsive interaction between the Li electron and these organic compounds.

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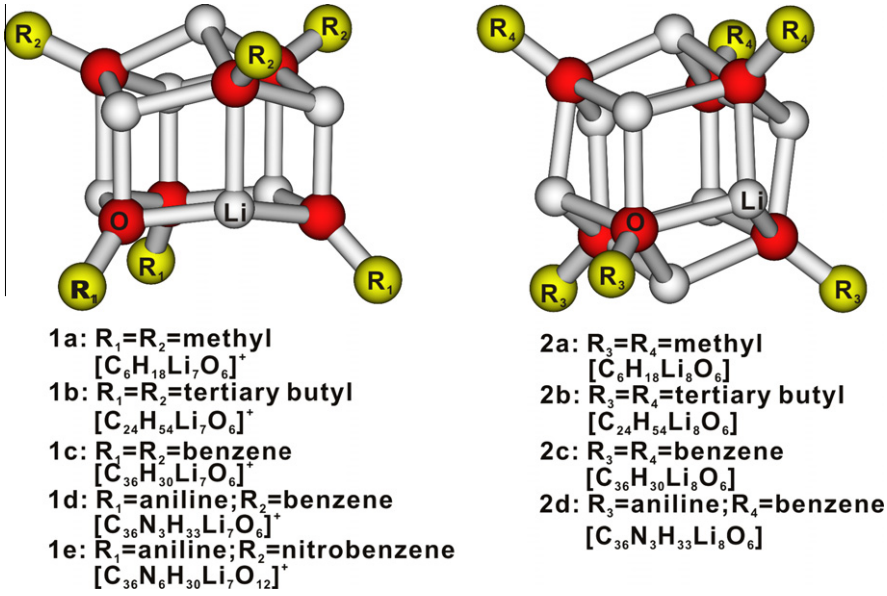

Fig. 1. Calculated equilibrium structures and their chemical formulas of the investigated compounds.

Although synthesis of pure lithium tert-butoxide is difficult, hexameric units $Li_6(O^tBu)_6$ at least in the gas phase were obtained [24]. Recently, $[Li_7(O^tBu)_6]^+$ cation was synthesized and characterized by X-ray diffraction analysis, in which all lithium atoms are three-coordinate, displaying no additional short contacts – i.e. agostic interactions – to methyl groups [25]. Moreover, Davies et al. synthesized a novel compound containing Li_8O_6 as core, in which Li_8O_6 is a rhombic dodecahedral cluster with 14 vertices, 12 faces, and 24 edges [26]. The inorganic nature of Li_8O_6 core might enhance the stability of the material and be helpful for experimentalists to handle it at room temperature and/or to use experimental conditions which are not possible to pure organic compounds. Based on the above structures, we design a series compounds containing different conjugate bridges, donor and acceptor (Fig. 1). We hope that these compounds might possess the merits of both inorganic and organic material and offer some interesting new opportunities for nonlinear optical materials.

Recent studies show that density functional theory calculations are remarkably successful in predicting a wide range of problems in organometallic chemistry [27–33]. In this paper, with the help of quantum-chemical calculations, it is desirable to obtain the following information: (1) study the electron spectra character of these compounds; (2) determine the character of charge transfer; (3) predict the nonlinear optical properties and elucidate the structure–property relationships from the micromechanism.

2. Computational method

Geometrical optimization of the studied compounds without any symmetry constraint was carried out with the B3LYP [34] combinations of density functional theory (DFT) in the Gaussian 09 computational chemistry program [35]. The B3LYP functional is a combination of Becke's three-parameter hybrid exchange functional [18] and the Lee–Yang–Parr [36] correlation functional. Basis set of 6-311G* was applied to our studied compounds. B3LYP employing the 6-311G* basis set can well reproduce the experimental structures of lithium carbonate [37,38]. Time-dependent density functional (TD-DFT) calculations were carried out at the B3LYP/6-31G* level to determine the electronic transition energy, oscillator strength, and transition character. The polarizabilities and hyperpolarizability were calculated as performed in the Gaussian 09 program package. To evaluate electron correlation effects, the static second-order polarizability was also calculated at the second-order Møller–Plesset (MP2) level. The effects of different DFT functionals and basis sets on polarizabilities and hyperpolarizability are also discussed.

The average polarizability value α_s can be obtained from the following the formula:

$$\alpha_s = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{1}$$

In general, electric-field-induced second harmonic generation (EFISHG) and hyper-Rayleigh scattering (HRS) are the two main methods to determine the second-order NLO properties. Here, we focused on the HRS response of the studied compounds. In the case of plane-polarized incident light and observation made perpendicular to the propagation plane without polarization analysis of the scattered beam, the second-order NLO response that can be extracted from HRS data [39] can be described as:

$$\beta_{HRS}(-2\omega;\omega,\omega) = \sqrt{\{\langle\beta^2_{ZZZ}\rangle + \langle\beta^2_{XZZ}\rangle\}} \tag{2}$$

$\langle\beta^2_{ZZZ}\rangle$ and $\langle\beta^2_{XZZ}\rangle$ correspond to isotropic orientational averages of the β tensor components without assuming Kleinman's conditions [40] and are described as:

$$\begin{aligned}\langle\beta^2_{ZZZ}\rangle = {} & \frac{1}{7}\sum_{\xi}^{x,y,z}\beta^2_{\xi\xi\xi} + \frac{4}{35}\sum_{\xi}^{x,y,z}\beta^2_{\xi\xi\eta} + \frac{2}{35}\sum_{\xi\neq\eta}^{x,y,z}\beta_{\xi\xi\xi}\beta_{\xi\eta\eta} \\ & + \frac{4}{35}\sum_{\xi\neq\eta}^{x,y,z}\beta_{\eta\xi\xi}\beta_{\xi\xi\eta} + \frac{4}{35}\sum_{\xi\neq\eta}^{x,y,z}\beta_{\xi\xi\xi}\beta_{\eta\eta\xi} + \frac{1}{35}\sum_{\xi\neq\eta}^{x,y,z}\beta^2_{\eta\xi\xi} \\ & + \frac{4}{105}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta_{\xi\xi\eta}\beta_{\eta\xi_\zeta} + \frac{1}{105}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta_{\eta\xi\xi}\beta_{\eta\xi_\zeta} + \frac{4}{105}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta_{\xi\xi\eta}\beta_{\zeta\zeta\eta}\end{aligned} \tag{3}$$

$$\begin{aligned}\langle\beta^2_{XZZ}\rangle = {} & \frac{1}{35}\sum_{\xi}^{x,y,z}\beta^2_{\xi\xi\xi} + \frac{4}{105}\sum_{\xi\neq\eta}^{x,y,z}\beta_{\xi\xi\xi}\beta_{\xi\eta\eta} - \frac{2}{35}\sum_{\xi\neq\eta}^{x,y,z}\beta_{\xi\xi\xi}\beta_{\eta\eta_\xi} \\ & + \frac{8}{105}\sum_{\xi\neq\eta}^{x,y,z}\beta^2_{\xi\xi\eta} + \frac{3}{35}\sum_{\xi\neq\eta}^{x,y,z}\beta^2_{\xi\eta\eta} - \frac{2}{35}\sum_{\xi\neq\eta}^{x,y,z}\beta_{\xi\xi\eta}\beta_{\eta\xi\xi} \\ & + \frac{1}{35}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta_{\xi\xi\eta}\beta_{\eta\zeta\zeta} - \frac{2}{105}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta_{\xi\xi\zeta}\beta_{\eta\eta\zeta} - \frac{2}{105}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta_{\xi\xi\eta}\beta_{\eta\zeta\zeta} \\ & + \frac{2}{35}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta^2_{\xi\eta\zeta} - \frac{2}{105}\sum_{\xi\neq\eta\neq\zeta}^{x,y,z}\beta_{\xi\eta\zeta}\beta_{\eta\xi\xi}\end{aligned} \tag{4}$$