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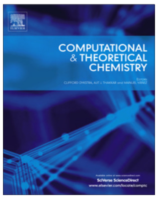

The structure and large nonlinear optical properties of a novel octupolar electride Li@3^6Adz

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ABSTRACT

Based on the synthesized H@3^6Adz (3^6Adz = 3^6 adamanzane), a new class of three-dimensional (3D) octupolar molecule Li@3^6Adz with electride characteristics is first designed and studied with theoretical tools, in which the electron of the encapsulated Li atom is extruded from the cage of 3^6Adz forming diffused excess electron. Due to S_4 symmetry, Li@3^6Adz only has the octupolar hyperpolarizability ($\beta_{J=3}$) up to 1787 × 10^{-30} esu at the restricted open-shell second-order Møller–Plesset (ROMP2) level, whose β is about 1787 times more than that (1 × 10^{-30} esu) of its analogue (H@3^6Adz). Interestingly, we find that both Li@3^6Adz has a very low ionization potential (1.84 eV) which can be seen as superalkalies. The present investigations will enrich the concept of 3D octupolar molecules for high-performance NLO materials and offer a method to construct superalkalies.

1. Introduction

The design and development of molecular nonlinear optical (NLO) materials with high NLO activity have attracted considerable scientific interest because of their potential applications in photonic and electro-optical devices [1–11].

For years, the molecular engineering in second-order nonlinear optics has been mainly dominated in the D-π-A type dipolar molecules. Although optical polarizabilities change considerably when increasing the length of the π-electron bridge and the strength of the donor and acceptor groups [1,2], the dipolar molecule of D-π-A structures retains considerable drawbacks that dipole–dipole electrostatic interactions of these dipolar molecules often lead to the disappearance of second-order NLO response at bulk materials.

Besides dipolar molecules for NLO, the concept of octupolar molecule has been proposed by Zyss and Ledoux in early 1990s [5]. Following this, a variety of organic octupolar molecules have been designed and investigated [12–15], and made great progress at the molecular and macroscopic level. Recently, Brasselet et al. [16,17] have reported that 1,3,5-tricyano-2,4,6-tris(p-diethylaminostyryl)benzene (TTB) crystal has a non-centrosymmetric octupolar structure and exhibits large first hyperpolarizability in bulk. In general, the macroscopic symmetry for crystals is often different from the single molecular one, which results in an obvious decrease in macroscopic NLO response. However, the TTB crystal does not suffer from such drawbacks, exhibiting the advantage of octupolar molecules. Besides crystal engineering [18], other different strategies have also been proposed to obtain a significant bulk second-order optical nonlinearity, by the non-centrosymmetric alignment of octupoles such as optical poling in polymers [19] and supramolecular arrangement [20–22]. Bulks are comprise of small units of octupolar molecules, and thus designing and developing new type octupolar molecules with high NLO activity is meaningful to the development of nonlinear optics. More recently, a lot of octupolar metallic complexes are reported, such as D_3 (Fe^{II}, Ru^{II}, Zn^{II}, Hg^{II}) and D_{2d} (Cu^{I}, Ag^{I}, Zn^{II}) octupolar metal complexes that feature different functionalized bipyridyl ligands [23,24]. In this aspect, Lin et al. [25–28] and Le Bozec groups [24,29–33] have done a lot of excellent works. In addition, Hirel et al. have recently designed and obtained an efficient second-order octupole whose structure is probably the closest yet reported to the true octupolar cube, ABAB homoleptic bis(phthalocyaninato)lutetium(III) complex [34].

On the other hand, electrides synthesized in experiment is a novel ionic salt in which anionic sites are occupied solely by electrons. And Electrides are strongly reducing materials in which alkali metals (Li through Cs) ionize to form bound alkali cations and "excess" electrons [35–38]. With such a unique structure, electrides provide a rich area for theory and have broad or potential applications to chemical synthesis, catalysis, nanodevices, and functional materials [39–41]. Many theoretical studies have shown that excess electron can reduce the transition energy of crucial excited states and thus lead to large second-order NLO responses

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[42–47]. Unfortunately, in the previous studies, all the designed electrides were based upon the dipolar molecule in nature. As aforementioned, when all such electrides are randomly oriented, the second-order NLO response will disappear because of forming centrosymmetric structure. Thus, in this paper, we first attempt to design and study a 3D octupolar electride Li@3^{6}Adz based upon the synthesized H@3^{6}Adz [39], in which 3^{6}Adz has a stable C–N framework at room temperature.

Our aim is to extend the concept of octupolar molecules, offer an interesting designing idea for three-dimension NLO molecules, and impetus the research of octupolar molecules for NLO.

2. Computational details

The geometric structures with all real frequencies for 3^{6}Adz, H@3^{6}Adz, and Li@3^{6}Adz are calculated at the MP2//6-31+G(d) level. And first hyperpolarizabilities are calculated at the MP2//6-311+G(d) level. The choice of basis sets will be discussed in Section 3.2.2. The interaction energies were corrected with the basis set superposition error (BSSE) using the counterpoise method of Boys and Bernardi [48]. The finite-field (FF) approach [49–54] has been applied to evaluate the tensor components of the static hyperpolarizabilities. It simply requires the evaluation of the system energy for different amplitudes of the applied external electric field and can therefore be applied to a broad range of methods. When a system is in a weak and stable applied electric field, its energy can be written as:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma \tag{1}$$

where E^0 is the molecular energy without the electric field, and F_α is an electric field component along α direction; μ, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the dipole moment, polarizability, and first hyperpolarizability, respectively. In this paper, we mainly focus on the β value.

For open-shell systems, UMP2 is usually very sensitive to spin contamination, which is an inherent feature of UHF wavefunctions on which UMP2 is based. Champagne et al. [52,53], have reported that for radical systems, the β values at the ROMP2 level are closer to those at the CCSD(T) level. Thus, the ROMP2 method is used to calculate first hyperpolarizabilities for our systems. All the calculations in this work were carried out using Gaussian 09 program packages [55].

3. Results and discussion

3.1. Geometrical characteristics

From Fig. 1 and Table 1, the four N atoms are distributed in form of tetrahedron in the cage of 3^{6}Adz, and the d_{N1-N2} and d_{N1-N3} distances are 3.055 Å and 3.333 Å, respectively. When H enters into the 3^{6}Adz cage, the cage expands and d_{N1-N2} and d_{N1-N3} in H@3^{6}Adz are increased to 3.281 and 3.536 Å, respectively. When Li entering enters into the 3^{6}Adz cage, the Li@3^{6}Adz cage should be expanded larger than H@3^{6}Adz because of the van der Waals radii (1.820 Å) of Li larger than that (1.200 Å) of the H atom, however, this is not the case here. The N–Li bond length (1.936 Å) in Li@3^{6}Adz is smaller than the N–H bond length (2.063 Å) in H@3^{6}Adz, and d_{N1-N2} (3.147 Å) and d_{N1-N3} (3.189 Å) in Li@3^{6}Adz are also shorter than d_{N1-N2} (3.281 Å) and d_{N1-N3} (3.536 Å) in H@3^{6}Adz. The reason is that the 2s electron of Li in Li@3^{6}Adz is extruded under the repulsion of lone pairs of four N atoms, relaxing the pressure. We will give an explanation in detail in the following part. The other parameters can be obtained in Supporting Information in which Cartesian coordinates of both Li@3^{6}Adz and H@3^{6}Adz are given.

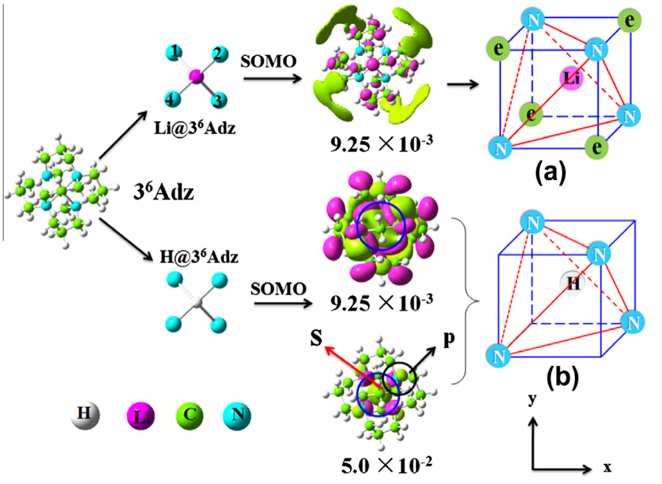

Fig. 1. The geometric structures of Li@3^{6}Adz and H@3^{6}Adz as well as their HOMOs with 9.25 × 10^{-3} and 5.0 × 10^{-2} au contour and the sketch map of dispersion of the excess electron. The letter p, s, and e denote the p orbital of the N atom, the s orbital of the H atom, and the diffused electron.

Table 1
Important parameter (Å), interaction energy with corrected BSSE (ΔE_{int}kcal/mol), first hyperpolarizability β (10^{-30} esu) and its tensor components, HOMO–LUMO gap (eV), and vertical ionization potential (VIP, eV) for 3^{6}Adz, H@3^{6}Adz, and Li@3^{6}Adz. $d_{N1\ldots N2}$ and $d_{N1\ldots N3}$ denote two different N–N distances ($d_{N1\ldots N2} = d_{N2\ldots N3} = d_{N3\ldots N4} = d_{N4\ldots N1}$, $d_{N1\ldots N3} = d_{N2\ldots N4}$ see Fig. 1).

Species	3^{6}Adz	H@3^{6}Adz	Li@3^{6}Adz
N–H(Li)		2.063	1.936
$d_{N1\ldots N2}$	3.055	3.281	3.147
d_{N1-N3}	3.333	3.536	3.189
ΔE_{int}		−33.58	−35.53
$\lvert\beta\rvert$		1	1787
β_{xyz}		0.4	729
HOMO–HOMO gap	10.17	7.30	1.64
VIP	6.09	3.02	1.84

3.2. Computational details

3.2.1. Suitable applied electric field (AEF)

It is important that the suitable applied electric field (AEF) is selected to calculate the intrinsic properties (first hyperpolarizability) of species containing solvent electron. Thus, the test of AEF is done from 0.0010 to 0.0030 au for Li@3^{6}Adz at the ROMP2/6-31+G* level of theory and is shown in Fig. S1. The result shows that the variation of β is very small and less than 1.0 × 10^{-30} esu in the range of 0.0010–0.0030 au of electric field, indicating this range of AEF can represent the intrinsic properties of the system. Thus we selected 0.0010 au of electric field, which is also default electric field and widely used to calculate first hyperpolarizability for containing excess electron systems.

3.2.2. Basis set effects

The choice of suitable basis set to calculate first hyperpolarizability is very important for systems containing loosely electrons. For Li@3^{6}Adz, effects of basis sets on first hyperpolarizability are studied at the ROMP2 level of theory with the different basis sets (see Table 2). From Table 2, we can see that first hyperpolarizabilities with diffuse functions (6-31+G(d) and 6-311+G(d)) are larger than those (6-31G(d) and 6-311G(d)) without diffuse functions. For Li@3^{6}Adz with excess electrons, it is very necessary to add diffuse functions for calculating first hyperpolarizabilities. In addition, from 6-31G(d) to 6-311G(d), first hyperpolarizabilities are not