



Theoretical studies of one- and two-photon absorption properties for three molecules with different centers (B and N) and peripheral substituted groups [N(CH₃)₂ and CN]

De-Ming Han^a, Ji-Kang Feng^{a,b,*}, Ai-Min Ren^a, Xiao-Hong Shang^b, Xiao-Juan Liu^c

^a State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

^b The College of Chemistry, Jilin University, Changchun 130023, China

^c State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

ARTICLE INFO

Article history:

Received 27 April 2008

Received in revised form

11 February 2009

Accepted 24 February 2009

Available online 21 March 2009

Keywords:

Two-photon absorption

Triazole

ZINDO

ABSTRACT

Three molecules with different centers (boron and nitrogen) and peripheral substituted groups [N(CH₃)₂ and CN] have been theoretically studied with B3LYP/6-31G(d) associated with ZINDO and sum-over-states methods. The maximum two-photon absorption cross-section δ_{\max} of the molecule with boron (B) center and N(CH₃)₂ peripheral group is larger than that of the molecule with nitrogen (N) center and N(CH₃)₂ peripheral group. As for the two molecules with N center, the δ_{\max} is obviously increased with the change from N(CH₃)₂ to CN group. This indicates that the large intramolecular charge transfer is in favor of the TPA response.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Two-photon absorption (TPA) was one of the nonlinear optical (NLO) phenomena observed experimentally. It is a process in which an atom or a molecule simultaneously absorbs two photons, which can have the same or different energies [1]. Molecules with large TPA responses are in great demand for various applications, including three-dimensional (3D) optical data storage, 3D optical imaging for biological systems, 3D microfabrication, optical power limiting and so on [2–4]. Recently, several design approaches have been reported for the synthesis of organic molecules with large TPA cross-sections. Albota et al. [5] investigated a series of linear (dipolar and quadrupolar) molecules with different D/A combinations attached to a π center (D = donor, A = acceptor). Cho et al. [6] have shown theoretically that, in branched molecule, the TPA cross-section increased as the strength of the donor–acceptor interaction increases. Some reports are available describing the effect of metal ions on TPA-active organic molecules [7,8]. In the early 1990s, Zyss and Ledoux [9] recognized that octupolar molecule is a new field of research in nonlinear optics. Recent works [10,11] have confirmed that octupolar structures are attractive materials for third-order

NLO application, including TPA. In recent years, our group has investigated the one- and two-photon absorption properties of some three-coordinate compounds [12,13].

It is interesting that Blanchard-Desce and co-workers [14] have synthesized and investigated some multipolar derivatives built from triazole moieties, which combine full transparency and strong TPA in the visible region. In general, the different central atoms and peripheral substituted groups have important effect on TPA response. So, in this paper, we design and study three molecules built from triazole moieties and with different centers (boron and nitrogen) and peripheral substituted groups [N(CH₃)₂ and CN]. Apparently, the C_{3h} point group of these molecules deviates from these types about purely octupolar molecules [9]; thus these molecules can be called pseudo-octupolar molecules. The one- and two-photon absorption properties for these pseudo-octupolar molecules have been theoretically investigated on the basis of geometrical structures optimized by the B3LYP/6-31G(d) level.

2. Theoretical methodology

In this paper, the molecular equilibrium geometries are calculated using the density functional theory with the B3LYP functional and the 6-31G(d) basis set. Then the property of electronic excited states was obtained by 196 single-electron excitation and 11 double-electron excitation configuration interactions using the ZINDO method. Furthermore, either UV–vis

* Corresponding author at: State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China. Tel.: +86 431 88499856; fax: +86 431 88498026.

E-mail address: jikangf@yahoo.com (J.-K. Feng).

(ground-state one-photon absorption) spectra or the transition dipole moment and the corresponding transition energy that were needed to predict TPA properties were provided. Then according to the formula for calculating TPA cross-section and sum-over-states (SOS) expression [15], the second hyperpolarizability γ and TPA cross-section δ were calculated.

3. Results and discussions

3.1. Geometry optimization and electronic structure

These pseudo-octupolar molecules investigated are shown in Fig. 1. The geometric structures are optimized using the Gaussian 03 program with a 6-31G(d) basis set at the B3LYP level. The optimized results show that all of these compounds with a propeller-like structure possess C_{3h} point symmetry. Table 1 lists the energies of some Kohn–Sham frontier orbitals obtained by the B3LYP/6-31G(d) method, which have important contributions to the low-lying state transitions. First, comparing the frontier orbitals of B-1 and N-1, it can be found that the HOMO of B-1 is degenerate with the next occupied orbital, while the HOMO orbital in N-1 is separated from the next occupied orbital with a comparatively large energy gap. In addition, the LUMO in N-1 is degenerate with the LUMO+1, while the LUMO in B-1 is separated

from the LUMO+1 with a large energy gap. As seen from Table 1, the ΔE_{H-L} (energy gaps between HOMO and LUMO) are 3.13362 and 3.99784 eV for molecules B-1 and N-1, respectively. It should be noticed that substitution of B with N makes the energy gap enlarged, which will further have effect on the absorption properties. Second, observing the frontier orbitals of N-2, one can find that the LUMO and LUMO+1 are degenerate with each other, while there is a large energy gap between the HOMO and the HOMO–1. Besides, the ΔE_{H-L} is smaller than that of N-1, which is due to their different peripheral substituted groups.

3.2. One-photon absorption

The OPA properties of the molecules have been calculated by using the ZINDO method on the basis of geometrical structures optimized by the B3LYP/6-31G(d) level. In Table 2, we list the calculated wavelength $\lambda_{\max}^{(1)}$, oscillator strength f and the nature of the transition for the maximal OPA of every molecule. All the studied molecules have two degenerate excited states, possessing the same intensity since their symmetry is C_{3h} . Note that for the N-1 molecule, the wavelength value of the maximum OPA peak is 343.8 nm, which is very close to the experimental values—347 nm [14].

For the molecules of B-1 and N-1, the $\lambda_{\max}^{(1)}$ is also obviously blueshifted as the oscillator strength f decreases from 1.35915 (B-1) to 1.01279 (N-1). For the molecules of N-1 and N-2, one can find that the oscillator strength f is slightly decreased from 1.01279 for N-1 to 1.00495 for N-2. And the $\lambda_{\max}^{(1)}$ is also blueshifted from 343.8 nm for N-1 to 330.4 nm for N-2. It indicates that different substituted groups have varied effect on the oscillator strength and the position of the maximum OPA. Herein, the charge transfer characters during the OPA are investigated. We have drawn the orbital contour plots of B-1 as an example to show the charge transfer direction in Fig. 2. For the B-1, HOMO \rightarrow LUMO and HOMO–1 \rightarrow LUMO are the important components of the transition nature. Thus, Fig. 2 shows only the orbital contour plots of HOMO–1, HOMO and LUMO. One can find that the charge densities of HOMO–1 and HOMO are mainly distributed on the branch parts, while the charge density of LUMO has many contributions from the central moieties. This indicates that in B-1 molecule, the B atom acts as an acceptor, and the OPA is due to the charge transfer from the branch parts to the central ones. Moreover, for the molecules investigated, we can analyze the electron density quantitatively by calculating the Mulliken charge on the center atoms in their ground [$Q(S_0)$] and excited states [$Q(S_n)$], and the charge changes (ΔQ) during the transition. The calculated results are listed in Table 3. Molecule B-1 has positive net charges (0.148944) in the ground state, while the molecules with N as center (molecules N-1 and N-2) have negative net charges in their ground state (the net charges are –0.187924 and –0.187169 for N-1 and N-2, respectively); this can be explained from their different Pauling's electronegativity (2.04 for B and 3.04 for N). In the excited state, the net charges on the center atoms are –0.090847, –0.158771 and –0.149622 for B-1, N-1 and N-2, respectively. So the net charge changes ΔQ during the

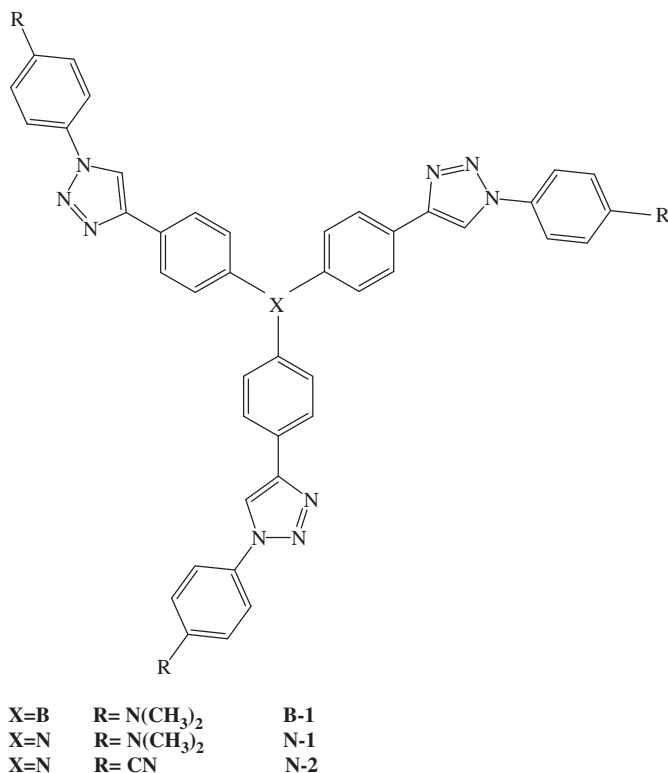


Fig. 1. The investigated molecules.

Table 1
Energies (eV) of some Kohn–Sham frontier orbitals HOMO– n and LUMO+ n ($n = 0, 1, 2$ and 3).

Molecules	HOMO–3	HOMO–2	HOMO–1	HOMO	LUMO	LUMO+1	LUMO+2	LUMO+3	ΔE_{H-L}
B-1	–5.81064	–5.1905	–5.13417	–5.13417	–2.00055	–0.74504	–0.74504	–0.6234	3.13362
N-1	–5.31295	–5.1388	–5.1388	–4.80682	–0.80898	–0.80898	–0.63157	–0.41279	3.99784
N-2	–7.07187	–6.58479	–6.58479	–5.5954	–2.20572	–2.20572	–2.16681	–1.32164	3.38968

Download English Version:

<https://daneshyari.com/en/article/5403073>

Download Persian Version:

<https://daneshyari.com/article/5403073>

[Daneshyari.com](https://daneshyari.com)