Ion–π interaction in impacting the nonlinear optical properties of ion–buckybowl complexes

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ABSTRACT

Ion–buckybowl complexes have received considerable attention in modern chemical research due to its fundamental and practical importance. Herein, we performed density functional theory (DFT) to calculate the geometical structure, binding interactions, dipole moments and the first hyperpolarizabilities (β_{tot}) of ion–buckybowl complexes (ions are Cl^- and Na^+, buckybowls are quadrannulene, corannulene and sumanene). It is found that the stabilities of ion–buckybowl compounds primarily originate from the interaction energy, which was proved by a new isomerization energy decomposition analysis approach. Plots of reduced density gradient mirror the ion–π weak interaction has been formed between the ions and buckybowls. Significantly, the buckybowl subunits cannot effectively impact the nonlinear optical (NLO), but the kind of ion has marked influence on the second-order NLO responses. The β_{tot} values of Cl^-–buckybowl complexes are all larger as compared to that of Na^+–buckybowl complexes, which is attributed to the large charge-transfer (CT) from Cl^- to buckybowl. Our present work will be beneficial for further theoretical and experimental studies on the NLO properties of ion–buckybowl compounds.

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1. Instruction

Buckybowls, bowl-shaped polycyclic aromatic hydrocarbons with carbon networks, have become a new research direction in recent years [1–22]. They retain the structural stabilities, having both the convex and concave π-faces and are available for coordination with cations and anions [5]. The smallest examples of these buckybowls are quadrannulene, corannulene, and sumanene. (Scheme 1) An elegant short synthesis of a quadrannulene derivative having a central four-membered ring had been reported by Bharat et al. [18]. It is flexible and permits the incorporation of substituents. Corannulene is the most famous one in the family of the buckybowls. Its unique open-end structures and the strained π conjugation make π bowls attractive to study [22]. In 1966, corannulene built around a central five-membered ring was first prepared by Barth and Lawton [23,24]. On the other hand, the first synthesis of sumanene with a central six-membered ring from nor-bornadiene was achieved in three or four steps under nonpyrolytic conditions [19]. The presence of three sp³-hybridized benzylic sites is one of the most characteristic structural features in sumanene, which allows the different chemistry from that of corannulene [22].

The study of the convex and concave ion binding in buckybowls has attracted significant interests both from experimental and theoretical scientific communities due to its fundamental and practical importance [4,11–13,15,21,25–29]. Many people studied cations binding in buckybowls [25–27]. Dunbar and Carrazana-García predicated that complexes formed by Na^+ and bowls were more stable outside the bowl [25,26]. Distance has significant influence on the interaction energy. So, the results of the stabilities will change with the change of the distances. Sastry concluded that metal ions in general prefer rim to the outside surface in buckybowls for the smaller Li^+ and Cu^+ ions while Na^+ and K^+ ions prefer hub binding to the inside surface in buckybowls [27].

Besides, others who studied anions binding in buckybowls showed that the most stable complexes arrangement corresponds in all cases to the anion located by the center of the inside face of the bowl (complexes formed by CN-substituted corannulene and sumanene with monovalent anions) [28]. Garcia-Novo et al. studied the interaction between anions and substituted molecular bowls [29]. They concluded that the complexes with anions were more stable inside bowls substituted with electron-withdrawing groups. Corannulene with chloride have been found to be more stable with the anion located on the rim of the bowl. The reference considered several starting structures, Side, Out1 and In. However, we want to draw a comparison between the ion inside and outside of the center ring of buckybowl (that authors did not considered). We will

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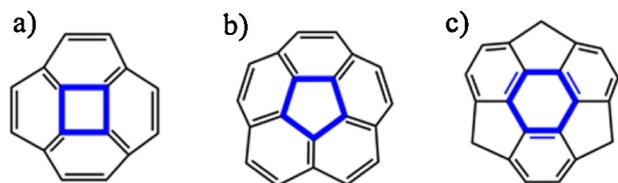
Scheme 1. Molecular structures of (a) quadrannulene (b) corannulene and (c) sumanene.

Fig. 1. The optimized structures of ion–buckybowl complexes with the ions inside of buckybowls (all hydrogen atoms are omitted for clarity).

Table 1
The relative energies (E_{rel}, kcal/mol) of the ion–buckybowl complexes obtained by the ωb97XD functional.

Complex	E_{rel}	Complex	E_{rel}
1a	0	1a′	–
1b	0	1b′	5.08
1c	0	1c′	7.56
2a	0	2a′	4.90
2b	0	2b′	3.17
2c	0	2c′	4.72

discuss the issue (ion–buckybowl) in different points of view from Ref. [29].

To the best of our knowledge, the second-order nonlinear optical (NLO) studies of ion–buckybowls are relatively lacking at present, especially theoretical study. These systems will be expected to be suitable models to explore the obvious charge-transfer (CT) behavior and the special ion–π interaction. Large NLO responses can be attributed to obvious charge-transfer [30,31]. Thus, ion–buckybowl complexes could be a new member of the family of NLO materials. Continuing our interest in the study of complexes with substantial NLO responses [3,32–37], a computational study of ion–buckybowl complexes (ions are Cl⁻ and Na⁺ for the reason that they are not just exemplified cation and anion. As cations, Na⁺ is the most representative of the alkali metal cations. The smallest Li⁺ polarises anions and gives its compounds a more covalent character. As anions, Cl⁻ was employed as representative of the simplest halogen anions. F⁻ was not considered since it binds to the molecular bowl in an almost covalent way as shown in other anion–π interactions [29], buckybowls are quadrannulene, corannulene and sumanene) have been presented in this work with the aim of gaining an insight into the relationship between the kind of buckybowls/ions and NLO properties. Based on this idea, their electronic structures, stabilities, interaction properties, dipole moments, and the first hyperpolarizabilities have been analyzed in this work.
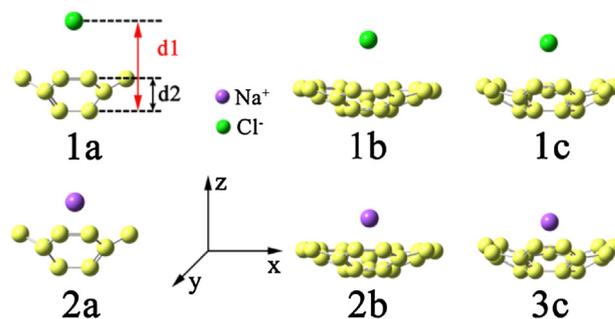
2. Computational details

The geometrical structures of the molecules were obtained at the ωB97XD/6–311 + G* level of theory with all real frequencies. The ωB97XD functional is the latest functional with long range corrections from Chai and Head-Gordon [38], which follows Grimme's work [39] for computing the empirical dispersion correction. What's more, this new functional is significantly superior for non-bonded interaction, and very similar in performance for bonded interaction [38]. Johnson et al. [40] developed an approach to detect the noncovalent interactions in real space, based on the electron density (ρ) and its derivatives. In this paper, we utilize this approach to identify the type of the noncovalent interactions in ion–buckybowl complexes.

The interaction energy (E_{int}) was systematically computed by using the same method as for the optimization of the structures. To correct the basis set superposition error (BSSE), the counterpoise (CP) procedure was used to calculate the interaction energy qualitatively [41,42]. The E_{int} can be expressed as the difference between the energies of fragements and the sum of energies of fragments according to:

$$E_{int}(AB) = E(AB)_{AB} - [E(A)_{AB} + E(B)_{AB}] \qquad (1)$$

For the calculation of the first hyperpolarizability, accurate results are essential. Therefore, three functionals were used here. The ωB97XD functional and another long-range corrected functional Becke–Lee–Yang–Parr (LC-BLYP) which has been found to be the more suitable functional for calculation of the first hyperpolarizabilities [43–45]. The third is Becke's half-and-half LYP (BH and HLY) functional which has been tested with notable success in

the calculation of molecular hyperpolarizability [46,47]. The first hyperpolarizability is given:

$$\beta_{tot} = \left(\beta_x^2 + \beta_y^2 + \beta_z^2 \right)^{1/2} \qquad (2)$$

where

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

The projection of β on dipole moment vector can be obtained by,

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

Where μ_i is the dipole moment along the direction of i.

Recently, time-dependent density functional theory (TD-DFT) method has been widely used to investigate the eletronic transition property due to its efficiency and accuracy [48–50]. To gain an insight into the description of the trend of the first hyperpolarizability, most important transitions and transition energies were calculated at the TD-ωB97XD/6–311 + G* level.

All calculations were carried out using Gaussian 09W package [51]. The electronic potential (ESP) were obtained by employing the Multiwfn software version 3.3.6 [52]. ESP was plotted using molekel4.3win32 [53]. The reduced density gradient (RDG) map was plotted using Multiwfn software version 3.3.6 [52] and VMD 1.9.1 [54].

3. Results and discussion

3.1. Geometical structure

The optimized structures of **1a**, **1b**, **1c** and **2a**, **2b**, **2c** (**1, 2** represent Cl⁻ and Na⁺ ion inside of buckybowls, respectively) are shown in the side view (Fig. 1.), while **1b′**, **1c′**, **2a′**, **2b′**, **2c′** (**1′, 2′** represent Cl⁻ and Na⁺ ion outside of buckybowls, respectively) are shown in Fig. S1. The stable geometrical structure of **1a′** has not been obtained by optimizing. The relative energies (E_{rel}) give a similar sequence for each of complexes with ions inside or outside (Table 1). That is, ions inside show much lower energies than the outside (Table S1). Thus, the former is more stable.