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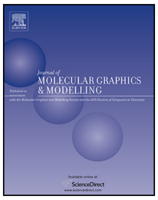

Theoretical investigation of the structures, stabilities, and NLO responses of calcium-doped pyridazine: Alkaline-earth-based alkaline salt electrides

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ABSTRACT

Currently, whether alkaline-earth-doped compounds with electride characteristics are novel candidates for high-performance nonlinear optical (NLO) materials is unknown. In this paper, using quantum chemical computations, we show that: when doping calcium atoms into a family of alkaline-substituted pyridazines, alkaline-earth-based alkaline salt electrides M-$H_3C_4N_2\cdots$Ca (M=H, Li, and K) with distended excess electron clouds are formed. Interestingly, from the triplet to the singlet state, the chemical valence of calcium atom changes from +1 to 0, and the dipole moment direction (μ_0) of the molecule reverses for each M-$H_3C_4N_2\cdots$Ca. Changing pyridazine from without ($H_4C_4N_2\cdots$Ca) to with one alkaline substituent (M-$H_3C_4N_2\cdots$Ca, M=Li and K), the ground state changes from the triplet to the singlet state. The alkaline earth metal doping effect (electride effect) and alkaline salt effect on the static first hyperpolarizabilities (β_0) demonstrates that (1) the β_0 value is increased approximately 1371-fold from 2 (pyridazine, $H_4C_4N_2$) to 2745 au (Ca-doped pyridazine, $H_4C_4N_2\cdots$Ca), (2) the β_0 value is increased approximately 1146-fold from 2 in pyridazine ($H_4C_4N_2$) to 2294 au in an Li-substituted pyridazine (Li-$H_3C_4N_2$), and (3) the β_0 value is increased 324-(M=Li) and 106-(M=K) fold from 826 (M=Li) and 2294 au (M=K) to 268,679 (M=Li) and 245,878 au (M=K), respectively, from the alkalized pyridazine (M-$H_3C_4N_2$) to the Ca-doped pyridazine (M-$H_3C_4N_2\cdots$Ca). These results may provide a new means for designing high-performance NLO materials.

1. Introduction

Recently, novel compounds with loosely bound excess electrons synthesized by Dye et al., called electrides, have attracted interest because of their broad potential applications in chemical synthesis, catalysis, nanodevices, and functional materials [1,2].

Until now, abundant strategies have been proposed for the design and synthesis of different types of non-linear optical (NLO) materials [3,4]. Among these strategies, doping is an important means of enhancing NLO responses. Recently, Li et al. proposed several alkali-doped compounds with excess electrons, for example Li@calix[4]pyrrole, Li-$H_3C_4N_2\cdots Na_2$, and Li_n-H-$(CF_2$-$CH_2)_3$-H ($n = 1, 2$), as novel, potential high-performance NLO materials [5–19]. These compounds have electride characteristics, in which the valence electron of an alkali atom is polarized by a ligand to become an excess electron. Considering the characteristics of diffuse excess electrons, Kirtman et al. [19] have determined and analyzed electronic and vibrational NLO properties of five representative electrides. Encapsulating LiCN$\cdots$Li within a boron nitride nanotube (as a protective shield) can enhance the stability of an unstable electride (LiCN$\cdots$Li) with an extremely large static first hyperpolarizability (β_0) value (310,196 au) [17].

Differing from the alkali metal atom with one electron in the valence orbital, an alkaline earth metal atom, *e.g.*, calcium atom, bears two valence electrons. According to the push-electron effect (polarization effect), the single electron of the alkali metal atom is easily pushed out to form an excess electron, resulting in the electride characteristics of an alkali-doped molecule [5–8]. Whether both valence electrons of the calcium atom can be pushed out to form an excess electron pair and whether the Ca-doped molecule exhibits alkaline-earth-based electride characteristics similar to the alkali-based electride is currently unknown. Recently, we have reported that the alkaline-earth-dopedalkaline-earth-doped compounds with unusual alkaline-earth-based alkalide features exhibit large β_0 (~2.76×10^4 au) [20]. Therefore, similar to the alkali-based electride and the alkaline-earth-based alkalide, can these alkaline-earth-based electride also exhibit large β_0 value? These are worth investigating.

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Recently, studies have shown that the lithium salt effect (lithiation effect) can greatly increases the β_0 value [8,21]. Moreover, for the short mono-lithiated zigzag-edged aza-Möbius graphene ribbon [2,7] isomers [12], we have studied the Li-orientation effects on the β_0 value. Introduction of hetero-aryl moieties into π-extended systems can modify and enhance a number of useful properties of advanced "electro-optic" materials. Recently Achelle et al. [22] have reviewed the optical properties of pyridazine derivatives. Considering both the lithiation effect and the electride effect, by doping two Na atoms into mono-lithiated pyridazine, Ma et al. [8] demonstrated that the new lithium salt electride, Li-$H_3C_4N_2\cdots Na_2$, has a very large β_0 value (1.41×10^6 au). Therefore, we considered it important to examine the combined alkaline earth metal salt and alkaline-earth-based electride effects on the β_0 value of a Ca-doped molecule.

In this paper, we studied an alkaline-earth-based electride originating from the alkaline-earth-doped pyridazine with and without an alkaline substituent (M-$H_3C_4N_2\cdots$Ca, M=H, Li, and K).

2. Computational methods

Recently, Ma et al. [8] have reported the β_0 value of the lithium salt electride, Li-$H_3C_4N_2\cdots Na_2$ at the second-order Møller-Plesset perturbation theory (MP2) level. Therefore, for the purpose of comparison, the geometries of the M-$H_3C_4N_2\cdots$Ca (M=H, Li, and K) molecules with all real frequencies were calculated at the MP2/6-311++G (3d, 2p) level.

The natural bond orbital (NBO) charges [23] and the vertical ionization energies (VIE(I & II)) were obtained at the MP2/6-311++G (3df, 2pd) level. The VIE(I & II) values were determined using the following formulae:

$$\mathrm{VIE(I)} = E[(\text{M-}H_3C_4N_2\cdots \mathrm{Ca})^+] - E[\text{M-}H_3C_4N_2\cdots \mathrm{Ca}] \quad (1)$$

$$\mathrm{VIE(II)} = E[(\text{M-}H_3C_4N_2\cdots \mathrm{Ca})^{2+}] - E[(\text{M-}H_3C_4N_2\cdots \mathrm{Ca})^+] \quad (2)$$

where $E[(\text{M-}H_3C_4N_2\cdots \mathrm{Ca})^+]$ and $E[(\text{M-}H_3C_4N_2\cdots \mathrm{Ca})^{2+}]$ are the energies of the $(\text{M-}H_3C_4N_2\cdots \mathrm{Ca})^+$ and $(\text{M-}H_3C_4N_2\cdots \mathrm{Ca})^{2+}$ cations (calculated with the same geometry of M-$H_3C_4N_2\cdots$Ca, respectively). The interaction energy (E_{int}) is the difference between the energy of M-$H_3C_4N_2\cdots$Ca and the sum of the energies of the metal calcium atom and the M-$H_3C_4N_2$ group, as illustrated by the following formula [24]:

$$E_{\mathrm{int}} = E_{\mathrm{AB}}(X_{\mathrm{AB}}) - E_{\mathrm{A}}(X_{\mathrm{AB}}) - E_{\mathrm{B}}(X_{\mathrm{AB}}) \quad (3)$$

The same basis set, X_{AB}, was used for both the moieties and the exohedral compound.

The deformation energy, E_{def}, of the pyridazine or that with an alkaline substituent (M-$H_3C_4N_2$) is defined as the energy difference between two M-$H_3C_4N_2$, in which one M-$H_3C_4N_2$ comes from the optimized M-$H_3C_4N_2\cdots$Ca and the other comes from the optimized undoped M-$H_3C_4N_2$. The E_{def} was also calculated at the MP2/6-311+G(3df, 2pd) level as the following formula:

$$E_{\mathrm{def}} = E[\text{M-}H_3C_4N_2]_{\text{opt M-}H_3C_4N_2\cdots \mathrm{Ca}} - E[\text{M-}H_3C_4N_2]_{\text{opt M-}H_3C_4N_2} \quad (4)$$

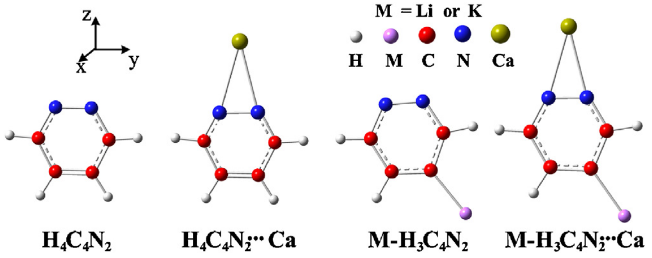

Fig. 1. Optimized geometries of the M-$H_3C_4N_2\cdots$Ca (M=H, Li, and K).

Previous studies [5–12] demonstrated that the MP2 method is suitable for calculating the first hyperpolarizability because the MP2 results are very close to those obtained by the more sophisticated correlation methods (for example, QCISD) with reasonable computation costs [5]. Therefore, the static first hyperpolarizabilities were calculated at the MP2/6-311++G (3df, 2pd) level within the finite field (FF) procedure. The dipole moment (μ_0) and polarizability (α_0) are defined as follows:

$$\mu_0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (5)$$

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (6)$$

The static first hyperpolarizability (β_0) is noted as,

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (7)$$

where $\beta_i = 3/5(\beta_{iii} + \beta_{ijj} + \beta_{ikk})$, $i, j, k = x, y, z$.

The spin contamination is negligible, as the expected value of the spin eigenvalue $\langle S^2 \rangle$ for each of triplet species is not large. The calculations were performed with the GAUSSIAN 09 (Revision A02) program package [25].

3. Results and discussion

3.1. Structure characteristics and stabilities

The optimized structures with all real frequencies of the M-$H_3C_4N_2\cdots$Ca (M=H, Li, and K) are shown in Fig. 1, and their geometric parameters are listed in Table 1.

For both singlet and triplet states, neither the alkaline earth metal doping effect nor the alkaline salt effect influences the structure of the pyridazine. The N—N bond length decreases (singlet M-$H_3C_4N_2\cdots$Ca) as calcium atom is doped into the pyridazine. Comparing the triplet M-$H_3C_4N_2\cdots$Ca with the corresponding singlet M-$H_3C_4N_2$ (M=H, Li, and K), the N—N bond length decreases (M=H) or increases (M=Li and K) slightly (<0.02 Å) as calcium atom is doped into the pyridazine. Comparing the alkaline salt (M-$H_3C_4N_2$) to the alkaline-earth-based alkaline salt electride (M-$H_3C_4N_2\cdots$Ca), the change of C—M bond lengths is also small (<0.05 Å). The C—M lengths in M-$H_3C_4N_2$ are 1.997 (M=Li) and 2.678 Å (M=K), and the lengths in M-$H_3C_4N_2\cdots$Ca are 2.016 (M=Li) and 2.718 Å (M=K). Therefore, calcium atom doping does not obviously change the C—M bond length. In addition, for each M-$H_3C_4N_2\cdots$Ca (M=H, Li, and K), the Ca—N length in triplet state is smaller than the corresponding length in the singlet state, and for each M-$H_3C_4N_2\cdots$Ca (M=Li and K), both the N—N and C—M lengths in the triplet state are larger than the corresponding lengths in the singlet state.

After comparing the total energies for each M-$H_3C_4N_2\cdots$Ca (M=H, Li, and K) in different spin states (Table 1), the energy of triplet structure is still lower than the singlet energy for M=H, and the singlet structure is still lower in energy than the triplet structure for M=Li and K, even though the energy difference between singlet and triplet states is small. Considering the electron correlation at higher levels, Table 1 shows that the singlet Li-$H_3C_4N_2\cdots$Ca is still lower in energy than the triplet one at each MP3/6-311++G(d,p)//MP4(DQ)/6-311++G(d,p), MP4(D)/6-311++G(d,p)//MP4(DQ)/6-311++G(d,p), and MP4(DQ)/6-311++G(d,p)//MP4(DQ)/6-311++G(d,p) level. At the same time, for the interaction energy (E_{int}) between the