



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 $M-H_3C_4N_2 \cdots Ca$ ($M=H, Li, \text{ and } K$) 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 alkalinized 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.

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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-doped alkaline-earth-doped compounds with unusual alkaline-earth-based alkalide features exhibit large β_0 ($\sim 2.76 \times 10^4$ 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 increase 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 electronegativity effect, by doping two Na atoms into mono-lithiated pyridazine, Ma et al. [8] demonstrated that the new lithium salt electride, $\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Na}_2$, 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 ($\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$, $\text{M}=\text{H}$, Li , and K).

2. Computational methods

Recently, Ma et al. [8] have reported the β_0 value of the lithium salt electride, $\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Na}_2$ at the second-order Møller-Plesset perturbation theory (MP2) level. Therefore, for the purpose of comparison, the geometries of the $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($\text{M}=\text{H}$, 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:

$$\text{VIE(I)} = E[(\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca})^+] - E[\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}] \quad (1)$$

$$\text{VIE(II)} = E[(\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca})^{2+}] - E[(\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca})^+] \quad (2)$$

where $E[(\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca})^+]$ and $E[(\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca})^{2+}]$ are the energies of the $(\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca})^+$ and $(\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca})^{2+}$ cations (calculated with the same geometry of $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$, respectively). The interaction energy (E_{int}) is the difference between the energy of $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ and the sum of the energies of the metal calcium atom and the $\text{M-H}_3\text{C}_4\text{N}_2$ group, as illustrated by the following formula [24]:

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

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 ($\text{M-H}_3\text{C}_4\text{N}_2$) is defined as the energy difference between two $\text{M-H}_3\text{C}_4\text{N}_2$, in which one $\text{M-H}_3\text{C}_4\text{N}_2$ comes from the optimized $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ and the other comes from the optimized undoped $\text{M-H}_3\text{C}_4\text{N}_2$. The E_{def} was also calculated at the MP2/6-311+G(3df, 2pd) level as the following formula:

$$E_{\text{def}} = E[\text{M-H}_3\text{C}_4\text{N}_2]_{\text{opt M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}} - E[\text{M-H}_3\text{C}_4\text{N}_2]_{\text{opt M-H}_3\text{C}_4\text{N}_2} \quad (4)$$

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

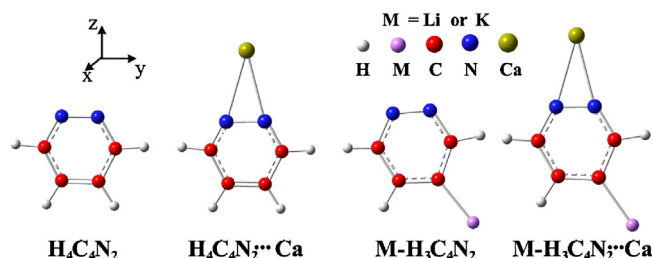


Fig. 1. Optimized geometries of the $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($\text{M}=\text{H}$, Li , and K).

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 $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($\text{M}=\text{H}$, 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 $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$) as calcium atom is doped into the pyridazine. Comparing the triplet $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ with the corresponding singlet $\text{M-H}_3\text{C}_4\text{N}_2$ ($\text{M}=\text{H}$, Li , and K), the N–N bond length decreases ($\text{M}=\text{H}$) or increases ($\text{M}=\text{Li}$ and K) slightly (<0.02 Å) as calcium atom is doped into the pyridazine. Comparing the alkaline salt ($\text{M-H}_3\text{C}_4\text{N}_2$) to the alkaline-earth-based alkaline salt electride ($\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$), the change of C–M bond lengths is also small (<0.05 Å). The C–M lengths in $\text{M-H}_3\text{C}_4\text{N}_2$ are 1.997 ($\text{M}=\text{Li}$) and 2.678 Å ($\text{M}=\text{K}$), and the lengths in $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ are 2.016 ($\text{M}=\text{Li}$) and 2.718 Å ($\text{M}=\text{K}$). Therefore, calcium atom doping does not obviously change the C–M bond length. In addition, for each $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($\text{M}=\text{H}$, Li , and K), the Ca–N length in triplet state is smaller than the corresponding length in the singlet state, and for each $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($\text{M}=\text{Li}$ 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 $\text{M-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($\text{M}=\text{H}$, Li , and K) in different spin states (Table 1), the energy of triplet structure is still lower than the singlet energy for $\text{M}=\text{H}$, and the singlet structure is still lower in energy than the triplet structure for $\text{M}=\text{Li}$ 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 $\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ 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

Table 1

Structural parameters (in Å) at the MP2/6-311++G(3d, 2p) level and total energies (E_{tot} , au), relative energies (E_{rel} , kcal/mol), interaction energy (E_{int}), deformation energies (E_{def} , kcal/mol), and vertical ionization energies (VIE(I&II), eV) for (M-H₃C₄N₂...Ca, M=H, Li, and K) at the MP2/6-311++G(3df, 2pd) level.

	H-H ₃ C ₄ N ₂ ...Ca		Li-H ₃ C ₄ N ₂ ...Ca		K-H ₃ C ₄ N ₂ ...Ca	
	Singlet	Triplet	Singlet	Triplet	Singlet	Triplet
Bond length						
Ca–N	2.644	2.280	2.576	2.363	2.554	2.355
	2.644	2.280	2.531	2.346	2.502	2.339
N–N	1.335	1.335	1.335	1.348	1.335	1.347
	(1.345)		(1.345)		(1.345)	
C–M	1.080	1.078	2.016	2.136	2.718	2.949
	(1.080)		(1.997)		(2.678)	
Energies						
E_{tot}	−940.7818	−940.7979	−947.6458	−947.6316	−1539.5692	−1539.5536
			−947.4455 ^a	−947.4291 ^a		
			−947.4767 ^b	−947.4574 ^b		
			−947.4448 ^c	−947.4272 ^c		
E_{rel}	0.0	−10.13	0.00	8.95	0.00	9.74
E_{int}	−8.46	−22.34	−15.40	−7.57	−18.40	−11.07
E_{def}	0.20	4.69	0.20	1.71	0.26	3.04
VIE(I)		5.037	3.699		3.468	
VIE(II)		8.538	8.759		8.478	

The values in the parentheses correspond to the M-H₃C₄N₂ molecules.

^a The values at the MP3/6-311++G(d,p)//MP4(DQ)/6-311++G(d,p) level.

^b The values at the MP4(D)/6-311++G(d,p)//MP4(DQ)/6-311++G(d,p) level.

^c The values at the MP4(DQ)/6-311++G(d,p)//MP4(DQ)/6-311++G(d,p) level.

calcium atom and pyridazine, the E_{int} of triplet structure is larger than that of the singlet one for M=H while the singlet structure is larger in energy than the triplet one for M=Li and K. These results indicate that doping a calcium atom into the pyridazine or the pyridazine with an alkaline substituent stabilizes the triplet state for the structure without an alkaline substituent (H₃C₄N₂...Ca) and the singlet state for the structure with an alkaline substituent (M-H₃C₄N₂...Ca (M=Li and K)). These results demonstrate a spin evolution of the ground state from the triplet to the singlet state when pyridazine is modified with an alkaline substituent.

To understand the stability of these molecules, the vertical ionization energies (VIE(I & II)), the interaction energy between the calcium atom and pyridazine (E_{int}), and the deformation energy (E_{def}) of the M-H₃C₄N₂ (M=Li and K) were calculated at the MP2/6-311++G(3df, 2pd) level. For both triplet and singlet states, the E_{int} of each structure is larger than the corresponding E_{def} . At the many-electron level, the VIE(I) and VIE(II) values of M-H₃C₄N₂...Ca are 3.468–5.037 eV and 8.478–8.759 eV, respectively (Table 1). These results show that M-H₃C₄N₂...Ca (M=Li and K) have certain stabilities.

Table 2

NBO charges and dipole moments (μ_0 , D) of different structures (M-H₃C₄N₂...Ca, M=H, Li, and K) at the MP2/6-311++G(3df, 2pd) level.

	H-H ₃ C ₄ N ₂ ...Ca		Li-H ₃ C ₄ N ₂ ...Ca		K-H ₃ C ₄ N ₂ ...Ca	
	Singlet	Triplet	Singlet	Triplet	Singlet	Triplet
NBO charge						
Ca	−0.017	0.887	−0.024	0.919	−0.028	0.916
N	−0.334	−0.617	−0.379	−0.498	−0.402	−0.509
	−0.334	−0.617	−0.378	−0.476	−0.392	−0.482
M	0.216	0.194	0.920	−0.059	0.945	−0.036
	(0.041)		(0.908)		(0.935)	
Dipole moment						
μ_x	0.000	0.000	0.001	−0.001	−0.001	0.001
μ_y	0.001	0.000	2.330	−5.083	1.437	2.217
μ_z	−11.910	0.297	−19.441	12.604	−23.260	12.791
μ_0	11.910	0.297	19.580	13.591	23.305	12.982

The values in the parentheses correspond to the M-H₃C₄N₂ molecules.

3.2. Alkaline-earth-based alkaline salt electrides

The NBO charges for M-H₃C₄N₂...Ca (M=H, Li, and K) at the MP2/6-311++G (3df, 2pd) level are listed in Table 2. For the singlet structures, the NBO charge of Ca in each M-H₃C₄N₂...Ca (M=H, Li, and K) is approximately 0 (Table 2). For all singlet M-H₃C₄N₂...Ca (M=H, Li, and K), the electron clouds of calcium atom in their corresponding highest occupied molecular orbitals (HOMOs) (see Fig. 2) are polarized by the two nitrogen atoms of the pyridazine to form distended excess electron clouds. That is to say, the two nitrogen atoms polarize the calcium atoms to form the excess electron pair. The VIE(I) values of 3.699 (M=Li) and 3.468 eV (M=K) for the M-H₃C₄N₂...Ca are smaller than the isolated calcium atom (6.113 eV) [26], and the VIE(II) values of 8.759 (M=Li) and 8.478 eV (M=K) are also smaller than the isolated calcium atom (11.872 eV) [26]. With regard to the related electrides with doped Li atoms, the VIE(I) values of M-H₃C₄N₂...Ca (M=Li and K) are lower than the electride of Li₃N₃Be (4.73 eV) [27], T-shaped Li₃OBeC₅H₅ (4.10–4.50 eV) [12] and (Li₃)⁺(SH)[−] (SH=LiF₂, BeF₃, and BF₄) (4.6–5.2 eV) [28]. Considering the distended excess electron clouds

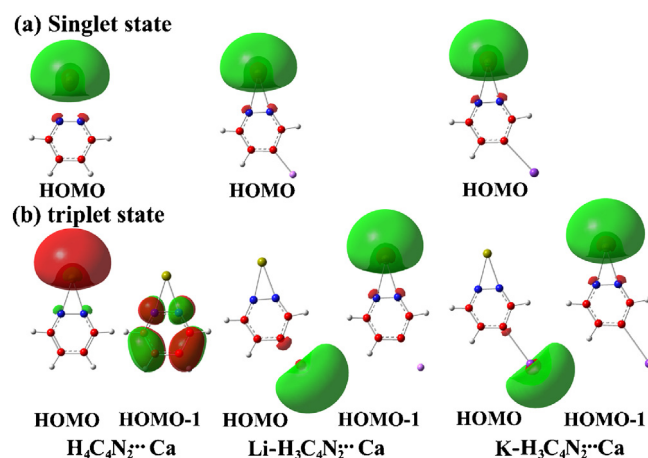


Fig. 2. Selected frontier molecular orbitals at the isovalue of 0.03 au for M-H₃C₄N₂...Ca (M=H, Li, and K).

(excess electron pair in HOMO) and the lower VIEs than the above reviewed electrides, these alkaline-earth-doped $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($M=\text{Li}$ and K) with singlet ground states are analogs of electrides and can be classified as alkaline-earth-based electrides.

In each of these alkaline-earth-based electrides, the two N atoms polarized the calcium atoms to form the excess electron pair. The NBO charges of two N atoms are related to the ability of the polarizing calcium atoms. For these molecules with a singlet state, the charge order of two N atoms is -0.334 ($\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$) < -0.379 or -0.378 ($\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$) < -0.402 or -0.392 ($\text{K-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$), and the charge order of two N atoms is -0.617 ($\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$) > -0.498 or -0.476 ($\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$) < -0.509 or -0.482 ($\text{K-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$) at the MP2/6-311++G(3df, 2pd) level for these molecules with a triplet state (Table 2).

For triplet structures, the NBO charge of M in each $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($M=\text{Li}$ and K) is approximately 0, and the NBO charge of the corresponding H atom in $\text{H-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ is small (0.194). For the triplet $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($M=\text{H}$, Li , and K), the electron clouds of M in their corresponding HOMOs (see Fig. 2) are pushed up by the pyridazine to form distended excess electron clouds. The VIE(I) value of 5.037 ($\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$) is close to that of the electride $(\text{Li}_3)^+(\text{BeF}_3)^-$ (5.103 eV) [28]. Therefore, these alkaline-earth-doped $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($M=\text{Li}$, and K) with triplet states are also electrides.

For each $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($M=\text{H}$, Li , and K), the NBO charges indicate that the valence of calcium atom and M metal atom in the singlet structures are 0 and +1, respectively, especially for $M=\text{Li}$ and K , and the valence of calcium atom and M metal atom in the triplet structure are +1 and 0, respectively, M , especially for $M=\text{Li}$ and K . The reversal of the dipole moment (μ_0) direction supports the different NBO charges between singlet and triplet states (see Table 2 and Fig. 1). The direction of μ_0 for each singlet structure of $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($M=\text{Li}$ and K) is defined from the calcium atom to the pyridazine ring ($-z$ direction) and is defined from the pyridazine ring to the calcium atom (z direction) for each triplet structure. Additionally, the HOMO of the singlet structure originates from the calcium atom, and the triplet structure originates from the Li or K atom. In addition, for the M ($M=\text{Li}$ and K), the NBO charge difference between $M\text{-H}_3\text{C}_4\text{N}_2$ and singlet $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ is very small, which suggests that the doping effect slightly influences the NBO charge of M .

3.3. Static polarizability and the first hyperpolarizability

The static polarizabilities (α_0) and β_0 of the stable structures, i.e., triplet $\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$ and singlet $M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ ($M=\text{Li}$ and K), were obtained at the MP2/6-311++G(3df, 2pd) level and are listed in Table 3. The order of α_0 values is 58 ($\text{H}_4\text{C}_4\text{N}_2$) < 72 ($\text{Li-H}_3\text{C}_4\text{N}_2$) < 84 ($\text{K-H}_3\text{C}_4\text{N}_2$) < 183 ($\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$) < 382 ($\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$) < 405 au ($\text{K-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$) (Table 3). By comparing $\text{H}_4\text{C}_4\text{N}_2$ with both $\text{Li-H}_3\text{C}_4\text{N}_2$ and $\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$, the lithium salt effect slightly increases the polarizability, and the alkaline earth metal doping effect (electride effect) increases the α_0 by approximately 6-fold compared to $\text{H}_4\text{C}_4\text{N}_2$. Similarly, the potassium salt effect slightly increases the polarizability, and the electride effect also largely increases the α_0 value from $\text{H}_4\text{C}_4\text{N}_2$ to $\text{K-H}_3\text{C}_4\text{N}_2$ and to $\text{K-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$.

The alkaline earth metal doping effect (electride effect) increases the β_0 value by approximately 1371-fold from 2 (pyridazine, $\text{H}_4\text{C}_4\text{N}_2$) to 2745 au (Ca-doped pyridazine, $\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$), and approximately from alkali-doped pyridazine ($M\text{-H}_3\text{C}_4\text{N}_2$) to the Ca-doped one ($M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$), the β_0 value 324-fold ($M=\text{Li}$) and 106-fold ($M=\text{K}$) from 826 ($M=\text{Li}$) and 2294 au ($M=\text{K}$) to 268,679 ($M=\text{Li}$) and 245,878 au ($M=\text{K}$), respectively, in alkali-doped pyridazine ($M\text{-H}_3\text{C}_4\text{N}_2$) versus the Ca-doped pyridazine ($M\text{-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$)

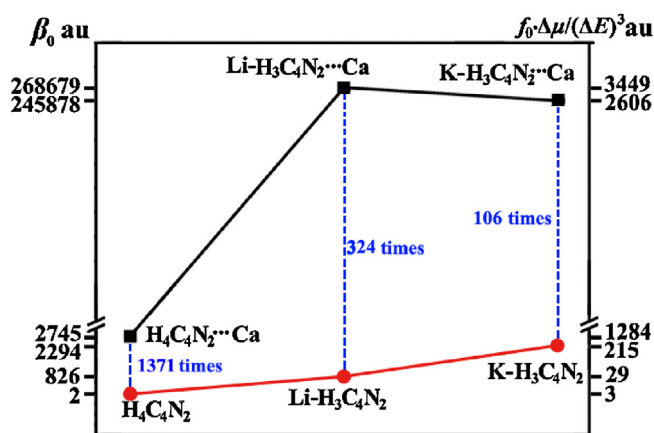


Fig. 3. Relationships among β_0 and $f_0 \cdot \Delta\mu / \Delta E^3$.

(Fig. 3). In addition, the change of the alkaline metal atom from Li to K does not affect the β_0 value. For the alkaline salt effect evidently, the β_0 value is increased by approximately 412-fold from 2 au in the pyridazine ($\text{H}_4\text{C}_4\text{N}_2$) to 826 au in the Li -substituted pyridazine ($\text{Li-H}_3\text{C}_4\text{N}_2$) and 1146-fold from 2 au in the pyridazine ($\text{H}_4\text{C}_4\text{N}_2$) to 2294 au in the K -substituted pyridazine ($\text{K-H}_3\text{C}_4\text{N}_2$). Combining the electride and the alkaline salt effects, the β_0 value is increased by 122,938-fold from 2 au in the pyridazine ($\text{H}_4\text{C}_4\text{N}_2$) to 268,679 au in $\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ and 134,338-fold from 2 au in the pyridazine ($\text{H}_4\text{C}_4\text{N}_2$) to 245,878 au in $\text{K-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$.

Although the β_0 values of the alkaline-earth-based alkaline salt electrides ($\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ and $\text{K-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$) are smaller than the analog of the reported lithium salt electride $\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Na}_2$ (1.41×10^6 au) [8], the β_0 values of the alkaline-earth-based alkaline salt electrides are still larger than those of the reported electrides of $\text{Li@calix[4]pyrrole}$ (7326 au) [6] and $\text{Li}_n\text{-H-(CF}_2\text{-CH}_2\text{)}_3\text{-H}$ ($n=1, 2$) (7.70×10^4 au) [7] and close to that of the alkali-doped $(M^+@n^6\text{ad}z)K^-$ ($M=\text{Li, Na, and K; } n=2, 3$) ($1.6 \times 10^5\text{--}3.2 \times 10^5$ au) [29]. These results suggested that, like alkaline metal atom doping, alkaline earth atom doping is an important method through which to enhance NLO responses.

According to the two-level expression proposed by Oudar and Chemla [30], the static first hyperpolarizability is proportional to the oscillator strength (f_0) and the difference of dipole moments between the ground state and the crucial excited state ($\Delta\mu$) but inversely proportional to the third power of the transition energy (ΔE) of the crucial excited state. Thus, the corresponding $\Delta\mu$, ΔE , f_0 , and $f_0 \cdot \Delta\mu / \Delta E^3$ values at the TD-LC-BLYP/6-311++G (d, p) level are also listed in Table 3. The $M\text{-H}_3\text{C}_4\text{N}_2$ ($M=\text{H}$ and Li) have large ΔE values of 7.071–7.487 eV, which may be the reason why they exhibit particularly small β_0 values. The $\text{K-H}_3\text{C}_4\text{N}_2$ and $\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$ have moderate ΔE values and some large f_0 ($\text{K-H}_3\text{C}_4\text{N}_2$) or $\Delta\mu$ ($\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$) values, which result in moderate β_0 values. For the alkaline-earth-doped species, $\text{Li-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ and $\text{K-H}_3\text{C}_4\text{N}_2\cdots\text{Ca}$ have large $\Delta\mu$ values of 8.688 and 6.669 au, respectively.

To understand the relative magnitude of those $\Delta\mu$ values, the changes of electron clouds in the crucial transitions is considered. These molecular orbital plots are depicted in Fig. 4. The charge transfer (CT) of the pyridazine ($\text{H}_4\text{C}_4\text{N}_2$) is not apparently exhibited. For both $M\text{-H}_3\text{C}_4\text{N}_2$ ($M=\text{Li}$ and K) and $\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$, the CTs are moderate, and the direction is near $-z$. The difference between $M\text{-H}_3\text{C}_4\text{N}_2$ ($M=\text{Li}$ and K) and $\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$ is only that the CT direction of $\text{Li-H}_3\text{C}_4\text{N}_2$ is from the pyridazine ring to the alkaline metal atom (M), and the CT direction of $\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$ is from the doped calcium atom to the pyridazine ring. Consequently, both $M\text{-H}_3\text{C}_4\text{N}_2$ ($M=\text{Li}$ and K) and $\text{H}_4\text{C}_4\text{N}_2\cdots\text{Ca}$ had moderate β_0 values. Combining

Table 3

Static mean polarizabilities (α_0), hyperpolarizabilities (β_0), oscillator strength (f_0), difference of dipole moment between the ground state and the crucial excited state ($\Delta\mu$), and transition energy (ΔE) for M-H₃C₄N₂···Ca and undoped M-H₃C₄N₂ (M=H, Li, and K).

	α_0 (au)	β_0 (au)	β_{zzz} (au)	f_0	$\Delta\mu$ (au)	ΔE (eV)	$f_0 \cdot \Delta\mu / (\Delta E)^3$
H ₄ C ₄ N ₂	58	2	20	0.433	0.130	7.457	3
H ₄ C ₄ N ₂ ···Ca	183	2745	4873	0.487	0.399	2.017	1284
Li-H ₃ C ₄ N ₂	72	826	946	0.146	3.434	7.071	29
Li-H ₃ C ₄ N ₂ ···Ca	382	268679	371098	0.139	8.688	1.916	3449
K-H ₃ C ₄ N ₂	84	2294	3195	0.110	5.562	3.858	215
K-H ₃ C ₄ N ₂ ···Ca	405	245878	386957	0.163	6.669	2.033	2606

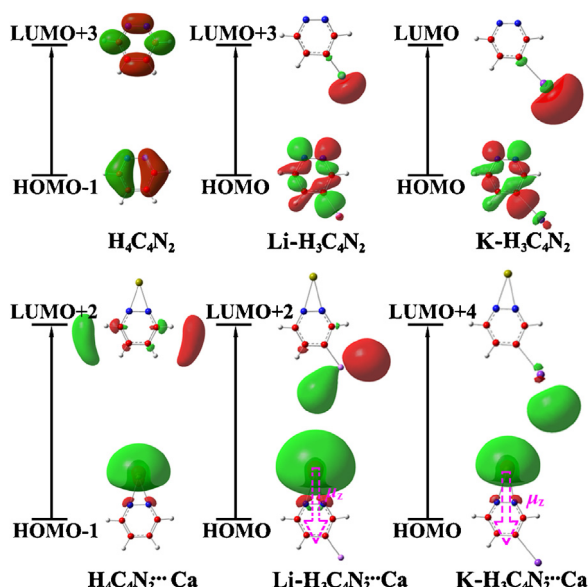


Fig. 4. Crucial transitions of M-H₃C₄N₂ and M-H₃C₄N₂···Ca (M=H, Li, and K).

the alkaline earth metal doping effect (electride effect) and the alkaline salt effect, the CT direction of M-H₃C₄N₂···Ca is from the doped Ca to the alkaline metal atom (M), which resulted in the largest CT among H₄C₄N₂, M-H₃C₄N₂, H₄C₄N₂···Ca, and M-H₃C₄N₂···Ca. For M-H₃C₄N₂, H₄C₄N₂···Ca, and M-H₃C₄N₂···Ca, the CT direction nearly corresponds with the μ_0 direction, which contributes greatly to the β_0 .

4. Conclusions

The present study explored new means of designing high-performance nonlinear optical materials by doping a calcium atom into a pyridazine with and without an alkaline substituent to form the alkaline-earth-based alkaline salt electriles M-H₃C₄N₂···Ca (M=H, Li, and K).

These alkaline-earth-doped compounds not only present unusual alkaline-earth-based electrile features but also exhibit large static first hyperpolarizabilities (β_0) up to 268,679 (Li-H₃C₄N₂···Ca) and 245,878 au (K-H₃C₄N₂···Ca), which suggests that combining the alkaline earth metal doping effect (electride effect) and the alkaline salt effect largely increases the β_0 value and that alkaline earth atom doping is an important method to enhance NLO responses. These results may provide new methods for designing high-performance nonlinear optical materials.

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