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REGULAR ARTICLE

Cis–trans isomerization and spin multiplicity dependences on the static first hyperpolarizability for the two-alkali-metal-doped saddle[4]pyrrole compounds

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Abstract Doping two alkali-metal atoms (Li and Na) into the saddle-shaped saddle[4]pyrrole forms four new two-alkali-metal-doped compounds with alkalide or electride characteristic. They are *cis*-LiNa(saddle[4]pyrrole) isomers **1**(singlet) and **2**(triplet), and *trans*-Li(saddle[4]pyrrole)Na isomers **3**(singlet) and **4**(triplet). The four structures with all-real frequencies are obtained at the density functional theory (DFT) B3LYP/6-311+G(d) level. All calculations of electric properties have been carried out at the second order Møller–Plesset perturbation theory (MP2) level. The order of the β_0 values is 3.54×10^3 for *trans*-**4**(triplet) $<1.51 \times 10^4$ for *cis*-**1**(singlet) $<3.57 \times 10^4$ for *cis*-**2**(triplet) $<2.34 \times 10^5$ a.u. for *trans*-**3**(singlet). The static first hyperpolarizability (β_0) depends on the *cis–trans* isomerization and spin multiplicity. The result demonstrates that the *cis–trans* isomerization and spin multiplicity controls of the second-order NLO response are possible.

Keywords *Cis–trans* isomerization · Spin multiplicity · Static first hyperpolarizability

1 Introduction

The research and design of materials with large nonlinear optical (NLO) response are of current interest because of the possibility of their use in photonic device applications such as optical data storage, optical communication, and optical limiting [1–7]. Organic π-conjugated polymers and oligomers [8, 9], organometallic compounds [10–12], and organometallic dendrimers [13] have shown promise in this regard.

Electrides are a novel kind of ionic salt in which the anionic sites are occupied by excess electrons, while alkalides are another ionic salt where the anionic sites are occupied by alkali-metal anions. In our previous work, the electride and alkalide molecules formed by doping alkali-metal atom(s) exhibit large static first hyperpolarizabilities and become a new type of potential NLO material [14–20]. The crucial role in the large static first hyperpolarizabilities is a new one played by excess electrons.

Recently, Nakano et al. reported the interesting spin multiplicity effect on the second hyperpolarizability for a series of such as phenalenyl radical systems [21–27]. It is demonstrated that the spin multiplicity control of the NLO response for organic radical systems is possible.

In our previous work, doing one and two alkali metal atoms into the calix[4]pyrrole forms electride and alkalide molecules, which exhibit large static first hyperpolarizabilities. The relative complexant saddle[4]pyrrole has higher symmetry (D_{2d}) to form fewer number of doped isomers and higher flexibility to bring larger NLO response. The complexant saddle[4]pyrrole is chosen in this work.

This paper aims at revealing the effects of the *cis–trans* isomerization and spin multiplicity on the static first hyperpolarizability for the new two-alkali-metal-doped

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saddle[4]pyrrole compounds with excess electrons, and providing a possibility of the controlling the second-order NLO response.

2 Computational details

The geometrical structures of the saddle[4]pyrrole and its four two-alkali-metal-doped compounds with all-real frequencies are obtained at the density functional theory (DFT) B3LYP/6-311+G(d) level. The static first hyperpolarizabilities are evaluated by the finite-field (FF) approach at the second order Møller–Plesset perturbation (MP2) level of theory. In our previous work for the alkali-metal doped molecule systems, with reasonable computation costs, the MP2 results are also close to those obtained from the more sophisticated correlation methods (for example, the quadratic configuration interaction with single and double excitation, QCISD) [15, 28]. The 6-311++G basis set for the C, N, and H atoms and the 6-311++G(3*df*) basis set for the alkali-metal atoms (Li and Na) were employed in this study as chosen in our previous work [16–18]. As one can see from Table S1 of the supplementary information, although the size of basis set 6-311++G is less than one-third of that of 6-311++G(2*d*, 2*p*), the β_0 value of 1.51×10^4 a.u. computed by the 6-311++G basis set is only 3.2% different from that of 1.46×10^4 a.u. computed by the 6-311++G(2*d*, 2*p*) for *cis*-LiNa(saddle[4]pyrrole) with the singlet state. In calculations, the $\langle S^2 \rangle$ values in MP2 wave functions are 2.0007 and 2.0013 for two triplet structures.

To find a proper applied electric field (AEF), the first hyperpolarizabilities (β_0) of *cis*-LiNa(saddle[4]pyrrole) with the singlet state are calculated at the MP2 level in a series of fields (see Table S2 in the supplementary information). The data of Table S2 shows that the β_0 values change slightly when the AEF varies from 0.0005 to 0.0015 a.u. Clearly, there is a plateau for β_0 in an AEF range from 0.0005 to 0.0015 a.u. Hereby, the AEF of 0.0010 a.u. is suitable in the calculation of β_0.

The finite-field (FF) approach is employed to the evaluation of β_0. A power series expansion convention (T convention [29]) is adopted for the definition of β_0. The total energy E of a molecular system in the presence of static electric field can be expressed as:

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

where E^0 is the molecular total energy without the electric field, and F_α the electric filed component along the α direction; μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the dipole moment, polarizability and the first hyperpolarizability, respectively.

The dipole moment (μ_0) and polarizability (α_0) are defined as follows:

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

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

The static first hyperpolarizability is noted as

$$\beta_0 = \left(\beta_x^2 + \beta_y^2 + \beta_z^2\right)^{1/2} \tag{4}$$

where

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

All calculations in this work were carried out using the GAUSSIAN 03 package [30]. The dimensional plots of molecular orbitals were generated with the Gauss View program (Gaussian, Inc., Pittsburgh, PA) [31].

3 Results and discussions

3.1 Equilibrium geometries and NBO charges

The geometrical structures of the saddle[4]pyrrole and its four two-alkali-metal-doped compounds are shown in Fig. 1. The important geometrical parameters are collected in Table 1.

The equilibrium geometry of the saddle[4]pyrrole has D_{2d} symmetry and adopts a saddle-shaped conformation with four pyrrole rings as shown in Fig. 1a, in which the four pyrrole rings are tilted up and down alternatively. By doping two alkali-metal atoms (Li and Na) into the saddle[4]pyrrole, **1**(singlet), **2**(triplet), **3**(singlet), and **4**(triplet) are formed (see Fig. 1b, c). As can be seen from Fig. 1b and c, for isomers **1** and **2**, the Li and Na atoms are located at the same sides of the saddle[4]pyrrole (denoted as *cis*-LiNa(saddle[4]pyrrole)), while for isomers **3** and **4**, the Li and Na atoms are located at the different sides of the saddle[4]pyrrole (denoted as *trans*-Li(saddle[4]pyrrole)Na).

Comparing with the complexant saddle[4]pyrrole, the N–N distances near the alkali-metal atoms of 6.282–6.407 Å in the four two-alkali-metal-doped saddle[4]pyrrole compounds are shorter than that of 6.694 Å in the saddle[4]pyrrole. The dihedral angles (θ) of 41–43° in the four doped compounds are larger than that of 36° in the saddle[4]pyrrole (see Fig. 1). This shows that doping alkali-metal atoms shorten the distance between the two pyrrole rings. The Li–Na distances in the *cis* isomers are 3.081 Å for singlet-**1** and 4.165 Å for triplet-**2**. With increasing of the spin multiplicity from the singlet state to the triplet state, the Li–Na distance is lengthened by

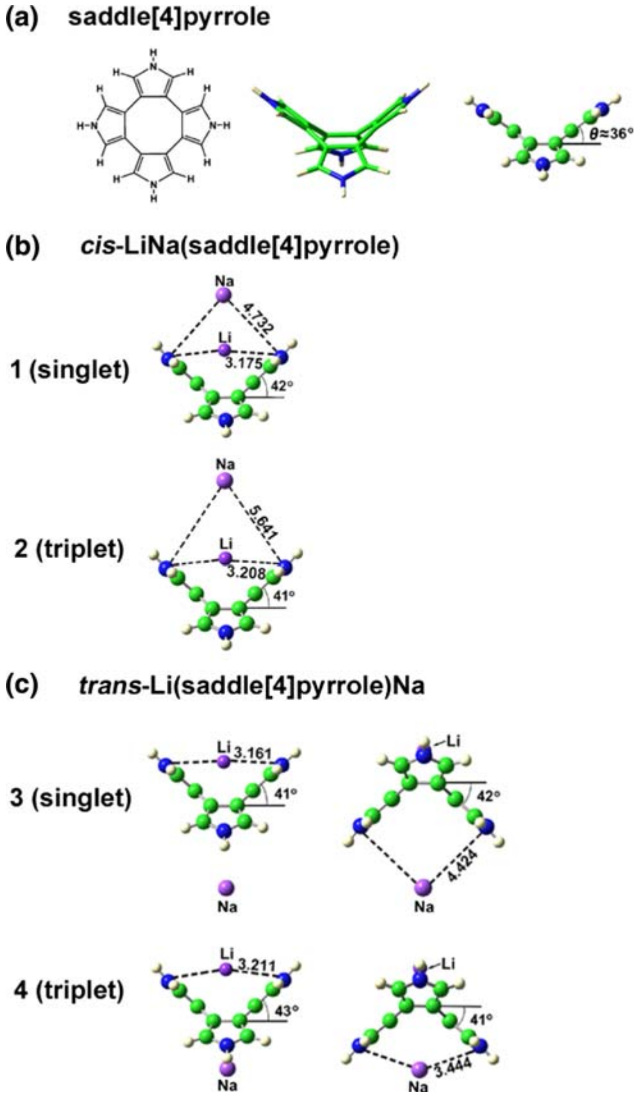


Fig. 1 The geometric structures of the saddle[4]pyrrole and its two-alkali-metal-doped compounds

1.084 Å. In contrast to the *cis* isomers, the Li–Na distances in the *trans* isomers are 6.868 Å for singlet-**3** and 5.423 Å for triplet-**4**. With increasing of the spin multiplicity from the singlet state to the triplet state, the Li–Na distance is shortened by 1.445 Å. This indicates that the Li–Na distance is related to the spin multiplicity in the *cis* and *trans* isomers. Moreover, the Li–Na distances of 3.081–4.165 Å for the *cis* isomers are shorter than those of 5.423–6.868 Å for the *trans* isomers.

The relative energies (E_{re}) of the four two-alkali-metal-doped saddle[4]pyrrole compounds at MP2/6-31+G(d) level are given in Table 1. It is shown that the *cis*-LiNa(saddle[4]pyrrole) isomers are more stable than the *trans*-Li(saddle[4]pyrrole)Na isomers, that is, the energies of the former are about 35 eV lower than those of the latter. In addition, for the *cis* isomers, its ground state is singlet because the energy of singlet-**1** is lower than that of triplet-**2** by 0.825 eV. For the *trans* isomers, the ground state is triplet because the energy of triplet-**4** is lower than that of singlet-**3** by 1.065 eV. Interestingly, the order of the stabilities is $\mathbf{1} > \mathbf{2} > \mathbf{4} > \mathbf{3}$, while the order of the Li–Na distances is $\mathbf{1} < \mathbf{2} < \mathbf{4} < \mathbf{3}$ (see Table 1). This indicates that the shorter Li–Na distance, the more stable the isomer is.

The NBO charges on the alkali-metal atoms (Li and Na) are also listed in Table 1, and the HOMO electron clouds are depicted in Fig. 2. The result shows that the **1**, **2**, and **3** have alkalide characteristic due to Na atoms with negative charges from the enwrapping of the excess electron clouds, while **4** has electride characteristic due to existing excess electron cloud by polarizing the Li and Na atoms.

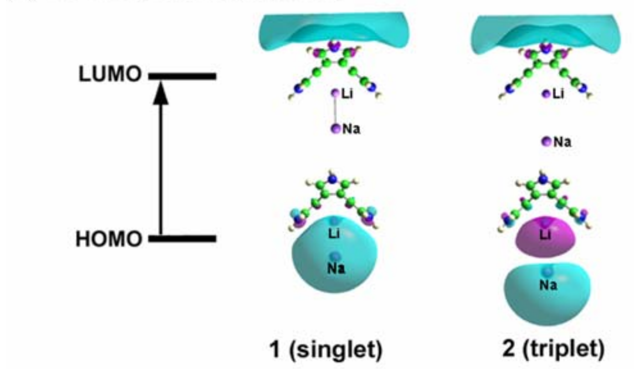
3.2 Static first hyperpolarizabilities

The electric properties of the two-alkali-metal-doped saddle[4]pyrrole compounds calculated at the MP2 level are

Table 1 The selected geometrical parameters (distance in Å, angle in °), NBO charge q, relative energy E_{re} (eV), and electronic spatial extent $\langle R^2 \rangle$ (a.u.)

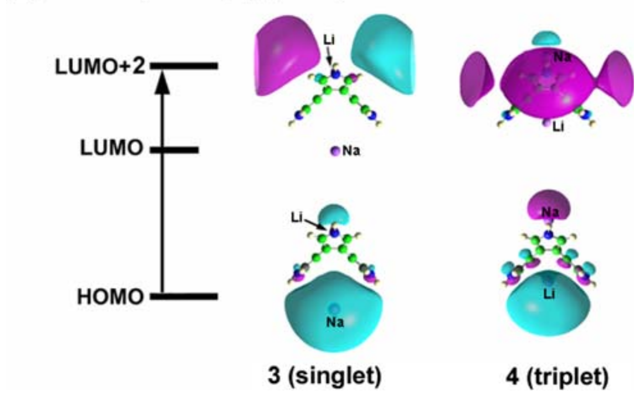
	Saddle[4]pyrrole	*cis*-LiNa(saddle[4]pyrrole)		*trans*-Li(saddle[4]pyrrole)Na	
		1(singlet)	**2**(triplet)	**3**(singlet)	**4**(triplet)
R(Li–N)		3.175	3.208	3.161	3.211
R(Na–N)		4.732	5.641	4.424	3.444
R(Li–Na)		3.081	4.165	6.868	5.423
R(N–N)	6.694	6.282	6.338	6.304	6.294
				6.314	6.407
θ	36	42	41	41	43
				42	41
q (Li)		0.428	0.077	0.858	0.024
q (Na)		−0.459	−0.079	−0.882	0.014
E_{re}		0	0.825	35.587	34.522
$\langle R^2 \rangle$		5,565	6,091	6,972	4,926
β_0	0	1.51×10^4	3.57×10^4	2.34×10^5	3.54×10^3

(a) ***cis*-LiNa(saddle[4]pyrrole)**



1 (singlet) **2 (triplet)**

(b) ***trans*-Li(saddle[4]pyrrole)Na**



3 (singlet) **4 (triplet)**

Fig. 2 Crucial transitions of the four two-alkali-metal-doped saddle[4]pyrrole compounds

given in Table 2. Doping two alkali-metal atoms (Li and Na) into the saddle[4]pyrrole greatly enhances the β_0 values from zero of the undoped saddle[4]pyrrole to 3.5×10^3 to 2.3×10^5 a.u. of the two-alkali-metal-doped saddle[4]pyrrole compounds. Thus, it is demonstrated that the effect of alkali-metal doping on β_0 is very considerable.

The order of the β_0 values is 3.54×10^3 for *trans*-**4**(triplet) $<1.51 \times 10^4$ for *cis*-**1**(singlet) $<3.57 \times 10^4$ for *cis*-**2**(triplet) $<2.34 \times 10^5$ a.u. for *trans*-**3**(singlet) (see Fig. 3). It is interesting to compare the β_0 values of the two-alkali-metal-doped saddle[4]pyrrole compounds with those of the other systems with large β_0 values. The β_0 values of 1.5×10^4 to 2.3×10^5 a.u. for **1**, **2**, and **3** with alkalide characteristic are larger than that of 1.4×10^4 a.u. for the Li(calix[4]pyrrole)Na with alkalide characteristic[17]. Taking into account the two complexants, calix[4]pyrrole and saddle[4]pyrrole, they both contain four pyrrole rings but they adopt two different conformations, i.e. calix-shape and saddle-shape, respectively. It is shown that the β_0 value is strongly related to the complexant shape. Furthermore, in comparison with the organometallic complex *trans*-[Ru(4-C = CHC_6H_4CHO) Cl(dppe)$_2$]PF_6 [32], the β_0 values of **1** and **2** is about 2–5 times larger than that of the complex.

As listed in Table 1, the β_0 values are related to the spin multiplicities and the atomic arrangements of the alkali-metal atoms for the two-alkali-metal-doped compounds. Four interesting effects of the *cis–trans* isomerization and spin multiplicity on β_0 have been observed.

(1) For either the *cis*-LiNa(saddle[4]pyrrole) or *trans*-Li(saddle[4]pyrrole)Na, the β_0 value is increased with the elongation of the Li–Na distance. For the *cis*-LiNa(saddle[4]pyrrole), the Li–Na distance is elongated from 3.081 Å for **1** to 4.165 Å for **2**, and the β_0 value is increased from 1.51×10^4 a.u. for **1** to 3.57×10^4 a.u. for **2**. For the *trans*-Li(saddle[4]pyrrole)Na, the Li–Na distance is elongated from 5.423 Å for **4** to 6.868 Å for **3**, and the β_0 value is hugely increased from 3.54×10^3 a.u. for **4** to 2.34×10^5 a.u. for **3**.

(2) For the singlet isomers, the β_0 value of 2.34×10^5 a.u. for *trans*-**3** is about 16 times enhanced as compared to that of 1.51×10^4 a.u. for *cis*-**1**. For the triplet isomers, the β_0 value of 3.57×10^4 a.u. for *cis*-**2** is about ten times enhanced as compared to that of 3.54×10^3 a.u. for *tran*-**4**. These features show the effect of the *cis–trans* isomerization on β_0.

Table 2 The dipole moment μ_0 (a.u.), polarizability α_0 (a.u.), first hyperpolarizability β_0 (a.u.), transition energy ΔE (eV), oscillator strength f_0, difference of dipole moment between the ground state and the crucial excited state $\Delta\mu$ (a.u.), and transition nature

	cis-LiNa(saddle[4]pyrrole)		*trans*-Li(saddle[4]pyrrole)Na	
	1(singlet)	**2**(triplet)	**3**(singlet)	**4**(triplet)
μ_0	2.732	5.063	8.976	0.329
α_0	455	559	2995	557
β_{zzz}	1.62×10^4	3.54×10^4	2.51×10^5	3.60×10^3
β_z	1.51×10^4	3.56×10^4	2.31×10^5	3.47×10^3
β_0	1.51×10^4	3.57×10^4	2.34×10^5	3.54×10^3
ΔE	2.114	1.710	0.830	1.769
f_0	0.353	0.282	0.185	0.113
$\Delta\mu$	1.774	3.966	5.011	1.312
$9\Delta\mu f_0/\Delta E^3$	1.21×10^4	4.05×10^4	2.95×10^5	4.83×10^3
Transition	HOMO → LUMO	HOMO → LUMO	HOMO → LUMO + 2	HOMO → LUMO + 2

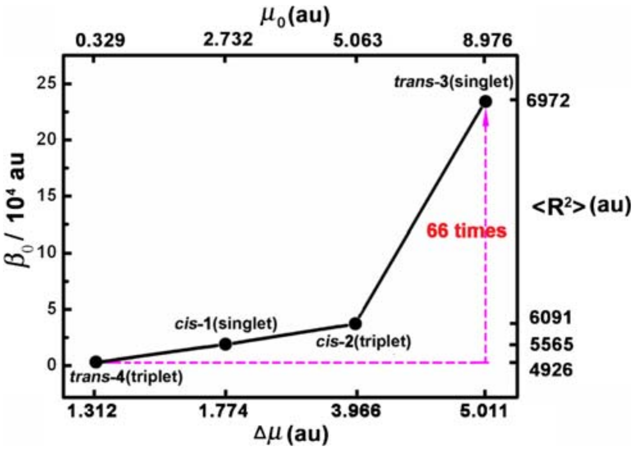


Fig. 3 The β_0 values versus to $\Delta\mu$, μ_0, and $\langle R^2 \rangle$ for the two-alkali-metal-doped saddle[4]pyrrole compounds

(3) For the *cis* isomers, the β_0 value of 3.57×10^4 a.u. for triplet-**2** is about two times larger than that of 1.51×10^4 a.u. for singlet-**1**. For the *trans* isomers, the β_0 value of 2.34×10^5 a.u. for singlet-**3** is about 66 times larger than that of 3.54×10^3 a.u. for triplet-**4** (see Fig. 3). Accordingly, the spin multiplicity significantly affects the β_0 value, especially in the *trans* isomers. Moreover, for either the *cis*-LiNa(saddle[4]pyrrole) or *trans*-Li(saddle[4]pyrrole)Na, the β_0 value of the ground state isomer is smaller than that of the excited state isomer. For example, for the *cis* isomers, the β_0 value of 1.51×10^4 a.u. for the ground state singlet-**1** is smaller than that of 3.57×10^4 a.u. for the excited state triplet-**2**.

(4) The β_0 values of **1**, **2**, and **3** with alkalide characteristic are larger than that of **4** with electride characteristic. Interestingly, a dependence on electronic spatial extent $\langle R^2 \rangle$ of the β_0 value is also presented (see Fig. 3). The electronic spatial extent $\langle R^2 \rangle$ characterizes the electron density volume around the molecule. The order of $\langle R^2 \rangle$ is $\mathbf{4} < \mathbf{1} < \mathbf{2} < \mathbf{3}$, which is identical with the order of β_0. Why is the electronic spatial extent $\langle R^2 \rangle$ for **4** with electride characteristic smaller than that for **1**, **2**, and **3** with alkalide characteristic? This is an interesting question. This reason is probably that, in **4** the anionic site is occupied by excess electron, while in **1**, **2**, and **3** the anionic sites are occupied by Na anions with enwrapped excess electron clouds. The excess electron cloud is expanded by Na atom core and becomes more diffuse exhibiting large $\langle R^2 \rangle$ value.

To understand the order of the first hyperpolarizabilities, we may consider the two-level model expression [33, 34].

$$\beta_0 \propto \beta_{zzz} = \frac{9\Delta\mu \cdot f_0}{\Delta E^3} \qquad (5)$$

where ΔE, f_0, and $\Delta\mu$ are the transition energy, oscillator strength, and the difference of dipole moment between the ground state and the crucial excited state[35], respectively. From Table 2, the β_{zzz} values obtained from Eq. 5 are good agreement with those from the finite-field (FF) approach. Equation 5 can be used to interpret the first hyperpolarizability.

The ΔE, f_0, and $\Delta\mu$ of the four two-alkali-metal-doped compounds are estimated by the configuration interaction with single excitations (CIS) method with the 6-31+G(d) basis set and listed in Table 2. From Eq. 5, the β_0 is proportional to $9\Delta\mu f_0/\Delta E^3$. The variation trend of $9\Delta\mu f_0/\Delta E^3$ is in agreement with that of β_0 (see Table 2). This shows that the order of the first hyperpolarizability (β_0) is jointly determined by the three quantities ($\Delta E, f_0$, and $\Delta\mu$). As can be seen from Table 2, the two-alkali-metal-doped compounds with excess electrons have the small ΔE of 0.830–2.114 eV due to the transitions of excess electrons (see Fig. 2), which relates to larger β_0 values. Notably, the order of $\Delta\mu$ is 1.312 for *trans*-**4**(triplet) <1.774 for *cis*-**1**(singlet) <3.966 for *cis*-**2**(triplet) <5.011 a.u. for *trans*-**3**(singlet), which is consistent with the order of β_0. This shows that the β_0 monotonously depends on the $\Delta\mu$ (see Fig. 3). Hence, the *cis–trans* isomerization and spin multiplicity controlling β_0 can be roughly understood by the controlling $\Delta\mu$ for the two-alkali-metal-doped systems.

To understand the relative magnitude of those $\Delta\mu$ values, we may consider those changes of electron clouds in the crucial transitions. The molecular orbital plots of the crucial transitions are depicted in Fig. 2. As can be seen, for *trans*-**3**(singlet), the charge transfer is large and long-range (about 6.9 Å) from the Na atom to the Li atom through the whole saddle[4]pyrrole molecule, so its $\Delta\mu$ value is large (5.011 a.u.). For both the *cis*-**1**(singlet) and *cis*-**2**(triplet), the charge transfer is obvious from the Li and Na atoms to the opposite side without the Li and Na atoms of the saddle[4]pyrrole through the saddle[4]pyrrole molecule. For *cis*-**1**(singlet), the center of HOMO electron cloud is located between Li and Na atoms. While, for *cis*-**2**(triplet), the center of HOMO electron cloud is located at near Na atom. For the distance of charge transfer, *cis*-**1**(singlet) is shorter than *cis*-**2**(triplet), then the $\Delta\mu$ value (1.774 a.u.) of *cis*-**1**(singlet) is smaller than that (3.966 a.u.) of *cis*-**2**(triplet). For *trans*-**4**(triplet), it has the smallest $\Delta\mu$ value (1.312 a.u.), as the distance of the main charge transfer is short from the Li atom to the saddle[4]pyrrole, but not through the saddle[4]pyrrole molecule.

Interestingly, it is found that the high spin state is smaller than low spin state for nonlinear optical (NLO) response. From Table 2, triplet-**4** (3.54×10^3) < singlet-**3** (2.34×10^5 a.u.) of *trans*-Li(saddle[4]pyrrole)Na for the first hyperpolarizabilities (β_0). This is an unusual case. While, triplet-**2** (3.57×10^4) > singlet-**1** (1.51×10^4 a.u.) for the *cis*-LiNa(saddle[4]pyrrole). This usual case, the high spin state > low spin state for NLO response has been reported [25, 26, 35]. For example, triplet (1.76×10^5) is larger than singlet (3.20×10^4 a.u.) for the alkalide anion Li_2F^- [36]. Both the *cis*-LiNa(saddle[4]pyrrole) and Li_2F^- with the singlet and triplet states have alkalide characteristic.

However, in *trans*-Li(saddle[4]pyrrole)Na, the high spin state is smaller than low spin state for NLO response. Why? This reason is that the change of spin multiplicity companies with the characteristic change between alkalide and electride for *trans*-Li(saddle[4]pyrrole)Na. The singlet-**3** with large negative charge of Na atom (−0.882) has alkalide characteristic and the triplet-**4** without negative charge of alkali metal atom has electride characteristic. From the HOMOs in Fig. 2, the excess electron cloud for the singlet-**3** with alkalide characteristic is more diffuse than that for the triplet-**4** with electride characteristic, which relates to singlet-**3** <triplet-**4** for ΔE and singlet-**3** >triplet-**4** for $\Delta\mu$. So, the β_0 value of the singlet-**3** with alkalide characteristic is larger than that of the triplet-**4** with electride characteristic.

For the usual case of the second hyperpolarizabilities, high spin state > low spin state is reported by Nakano and co-workers. The second hyperpolarizability increases with increasing spin multiplicity for the open-shell neutral π-conjugated C_5H_7 radical [25] and phenalenyl radical systems [26].

In addition, the order of μ_0 is 0.329 for *trans*-**4**(triplet) <2.732 for *cis*-**1**(singlet) <5.063 for *cis*-**2**(triplet) < 8.976 a.u. for *trans*-**3**(singlet), which is also identical with that of β_0. This implies that there exists relation between β_0 and μ_0. The μ_0 is the dipole moment of the ground state, while the $\Delta\mu$ related to the β_0 is the difference of dipole moment between the ground state and the crucial excited state. From Table 2 and Fig. 3, the corresponding $\Delta\mu$ varies monotonously with the μ_0. It is easy to understand that there exists monotonous relationship between the β_0 and μ_0.

4 Conclusion

In these doped systems with excess electrons, the effects of the *cis–trans* isomerization and spin multiplicity on the static first hyperpolarizability (β_0) are shown for two-alkali-metal-doped saddle[4]pyrrole compounds with alkalide or electride characteristic. These results demonstrate the possibility of the *cis–trans* isomerization and spin multiplicity controls of the second-order NLO response for the two-alkali-metal-doped compounds. The β_0 values of **1**, **2**, and **3** with alkalide characteristic are larger than that of **4** with electride characteristic. Interestingly, for the first hyperpolarizabilities (β_0) of *trans* isomers, low spin state (singlet-**3**) > high spin state (triplet-**4**) due to the characteristic change from alkalide to electride, which is different from the usual cases of *cis* isomers and reported alkalide anion Li_2F^- [36]. This work provides beneficial knowledge to design NLO materials.

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