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Structure and stability of hypervalent NLi_nNa_2 ($n = 1–4$) and related species at density functional theory level

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Abstract. A number of configurations of NLi_nNa_2 ($n = 1–4$) species were optimized using the B3LYP–density functional theory method; the 6-31G* basis set was used in this calculation. In order to study all possible dissociation energies, some related species such as NLi_2Na, $NLi_n(n = 1–4)$, $Li_n(n = 1, 2)$ and $Na_n(n = 1, 2)$ were also considered. Optimizations of these species were followed by fundamental frequency calculations at the same level. Global minima of these species were shown to adopt C_{2v}(NLi_4Na_2, NLi_2Na_2), D_{3h}(NLi_3Na_2) and C_s($NLiNa_2$ and NLi_2Na) configurations. All possible dissociation energies were obtained.

Key words: Hypervalent – Configuration – Stability – Bimetallic cluster

1 Introduction

Hyperalkali molecules with stoichiometries exceeding normal valent expectations are now well documented [1–12]. The molecules CLi_5, CLi_6, NLi_6, NLi_5, OLi_4, OLi_6, FLi_3, PLi_4, ONa_4, SLi_3, PLi_4, etc., were predicted computationally[1–6]. Experimentally, OLi_3[7], OLi_4 and OLi_5[8], ONa_3, ONa_4, OK_3 and OK_4[9], SLi_2 and SLi_4[10], and PLi_4[11] and CLi_6 [12] have been observed by mass spectroscopy. The stability of these hypervalent species is due to extra electrons which contribute to ligand–ligand bonding and the metallic "cage" around the central atom according to previous studies.

We have systematically studied the structures and stabilities of CLi_n, OLi_n, NLi_n and OK_n ($n = 2–6$) [13–16]. Since Na lies under Li in the same group, it should have similar properties in some circumstances. So we substituted a Na atom for a Li atom in NLi_n ($n = 4–6$) hyperlithium species and considered such molecules as NLi_4Na_2, NLi_3Na_2, NLi_2Na_2, $NLiNa_2$ and NLi_2Na, including the geometrical optimization, thermodynamic stability, bonding properties, etc. Vibrational frequencies were calculated to ensure the species were true minima. While there is no experimental information about these species, our results will be useful for experimental studies of such hypervalent species.

2 Computational details

The geometries of NLi_2Na, $NLiNa_2$, NLi_2Na_2, NLi_3Na_2, NLi_4Na_2 and related species were optimized employing an analytical gradient [17] with the 6-31G* basis set at B3LYP–density functional theory level [18]. Fundamental frequencies, normal coordinates and zero-point energies (ZPE) were calculated by the standard **FG**-matrix method [19]. All calculations were carried out with Gaussian 94 [20] on an SGI/O2 workstation.

3 Results and discussion

3.1 Dissociation energies and stabilities

The dissociation energies of the $NLi_nNa_{1–2}$($n = 1–4$) molecules are listed in Table 1 (all energies are ZPE-corrected). We discuss their energies and stabilities as follows.

NLi_2Na

We calculated two configurations of the NLi_2Na molecule: planar C_{2v} and pyramidal C_s species. The C_s form was optimized to be a true minimum according to the frequency calculation (with no imaginary frequency), while the C_{2v} form is a saddle point. The C_s structure of the NLi_2Na molecule is stable towards dissociation, and an energy of 38.01 kcal/mol is needed for the $NLi_2Na \rightarrow NLi_2 + Na$ reaction.

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Table 1. Dissociation energies of $NLi_nNa_2(n = 1–4)$ and related species (kcal/mol). All dissociation energies are calculated with zero-point-energy-corrected total energies. The *number* which follows the configuration of each molecule refers to the number appearing in Fig. 1

Dissociation reaction	Energy
NLi_2Na (C_s, 1) $\rightarrow$ NLi_2 (C_{2v}) + Na	38.01
$NLiNa_2$ (C_s, 3) $\rightarrow$ $NLi(C_{\infty v})$ + Na_2	108.04
NLi_2Na_2 (C_{2v}, 4) $\rightarrow$ NLi_2Na (C_s, 1) + Na	25.62
NLi_2Na_2 (C_{2v}, 4) $\rightarrow$ $NLiNa_2$ (C_s, 3) + Li	59.23
NLi_2Na_2 (C_{2v}, 4) $\rightarrow$ $NLi_2(C_{2v})$ + Na_2	67.32
NLi_2Na_2 (C_{2v}, 4) $\rightarrow$ NNa_2 (C_{2v}) + Li_2	87.13
NLi_3Na_2 (D_{3h}, 6) $\rightarrow$ NLi_2Na_2 (C_{2v}, 4) + Li	45.45
NLi_3Na_2 (D_{3h}, 6) $\rightarrow$ $NLiNa_2$ (C_s, 3) + Li_2	84.91
NLi_3Na_2 (D_{3h}, 6) $\rightarrow$ $NLi_3(D_{3h})$ + Na_2	42.58
NLi_4Na_2 (C_{2v}, 9) $\rightarrow$ NLi_3Na_2 (D_{3h}, 6) + Li	20.86
NLi_4Na_2 (C_{2v}, 9) $\rightarrow$ NLi_2Na_2 (C_{2v}, 4) + Li_2	46.54
NLi_4Na_2 (C_{2v}, 9) $\rightarrow$ $NLi_4(T_d)$ + Na_2	10.35

$NLiNa_2$

We also computed two configurations of the $NLiNa_2$ molecule: planar C_{2v} and pyramidal C_s species. The C_s form was optimized to be a true minimum according to the frequency calculation (with no imaginary frequency), while the C_{2v} form has an imaginary frequency of 92 $cm^{-1}(b_1)$. The C_s molecule of $NLiNa_2$ is stable towards dissociation, and an energy of 108.4 kcal/mol is needed for the $NLiNa_2 \rightarrow NLi + Na_2$ reaction.

NLi_2Na_2

Three configurations of NLi_2Na_2 were optimized and only two C_{2v} isomers are stable. The $NLi_2Na_2(C_{2v}, 4)$ form is a little more stable than the $NLi_2Na_2(C_{2v}, 5)$ one. We found out that Na atoms are weakly bonded to the central N atom because the $NLi_2Na_2(C_{2v}, 4)$ molecule needs nearly 34 kcal/mol more energy to release Li than Na species and 20 kcal/mol more energy to release Li_2 than Na_2 species.

NLi_3Na_2

Three configurations, D_{3h}, C_{2v} and C_s, were optimized for NLi_3Na_2. The D_{3h} form has a LiLiLi plane and the two Na atoms lie on the line vertical to the plane. The C_s form has a LiLiNa plane and other Li and Na lie on the line perpendicular to the plane. The results show that the three configurations are all stationary points on the potential-energy surface of NLi_3Na_2. The most stable one is the D_{3h} form and it is more stable than the C_{2v} and C_s ones by 3.02 and 3.18 kcal/mol, respectively. Apparently, the latter two are only local minima. From Table 1, we can see that NLi_3Na_2 (D_{3h}) is stable towards dissociation by losing Li, Li_2 and Na_2.

NLi_4Na_2

Two configurations, D_{4h} and C_{2v} were optimized to be stationary points for NLi_4Na_2. The D_{4h} form has a plane composed of four Li atoms and the two Na atoms lie on a line perpendicular to the plane. For the C_{2v} form, two Li and the two Na atoms lie in a certain plane and the other two Li atoms are located on a line perpendicular to the plane. The latter configuration is 12.83 kcal/mol more stable than the former. NLi_4Na_2 (C_{2v}) is stable towards dissociation by losing Li, Li_2 and Na_2 (Table 1). For the $NLi_4Na_2(C_{2v})$ molecule, nearly 36 kcal/mol more energy is needed to release Li_2 than Na_2 species, so we can say that Na atoms are not so strongly bonded to the central N atom as Li atoms.

3.2 Optimized geometries

The optimized bond lengths are shown in Fig. 1. From calculated bond lengths, we can see that along the series $NLi_2Na(NLiNa_2) \rightarrow NLi_2Na_2 \rightarrow NLi_3Na_2 \rightarrow NLi_4Na_2$ the bond lengths of N-Li and N-Na increase by about 0.4 Å step by step. This is different from the case of $CLi_nNa_2(n = 1–4)$, in which at coordination number $n+2 \le 4$, the bond lengths of C-Li and C-Na decrease step by step, while at $n + 2 > 4$, the bond lengths increase. This may result from the fact that for N-based clusters, the valence electron numbers are always equal to or larger than 8. For C-based clusters the case is a little different. At $n = 1$, the total valence electron number is 7, which is smaller than 8, while the valence electron numbers are equal to or larger than 8 as $n \ge 2$. So the latter case is the same as $NLi_nNa_2(n = 1–4)$.

3.3 Charge distributions and bonding

For the global minima of these species, charge distributions were calculated by Mulliken population analysis. The results are presented in Table 2, and the bond orders are shown in parentheses under the corresponding bond lengths in Fig. 1. Along the series of $NLiNa_2(NLi_2Na) \rightarrow NLi_2Na_2 \rightarrow NLi_3Na_2 \rightarrow NLi_4Na_2$, the bond orders of N-Li and N-Na decrease as 0.325(0.320) $\rightarrow$ 0.272 $\rightarrow$ 0.257 $\rightarrow$ 0.228, 0.151 and 0.215(0.225) $\rightarrow$ 0.128 $\rightarrow$ 0.06 $\rightarrow$ −0.010. This indicates that as one more Li atom is added, the bond order between the central N and ligand Li atoms is apparently lowered, and that is also true for the N-Na bond, while those between adjacent alkali atoms are increased. For example the Na-Na bond order increases from −0.125 in $NLiNa_2(C_s)$ to 0.240 in $NLi_4Na_2(C_{2v})$. So we believe that the added ligands do not connect directly with the central N atom, and extra electrons do not mainly contribute to bonding of N-Li, but to that of Li-Li and Li-Na.

Table 2. Charge distribution of $NLi_nNa_2(n = 1–4)$ and NLi_2Na species

Species	Q_{C}	Q_{Li}	Q_{Na}
NLi_2Na	−0.747	0.239	0.269
$NLiNa_2$	−0.726	0.258	0.234
NLi_2Na_2	−0.823	0.353	0.058
NLi_3Na_2	−0.845	0.713	−0.647
NLi_4Na_2	−0.908	0.610(Li_a) 0.267(Li_e)	−0.423

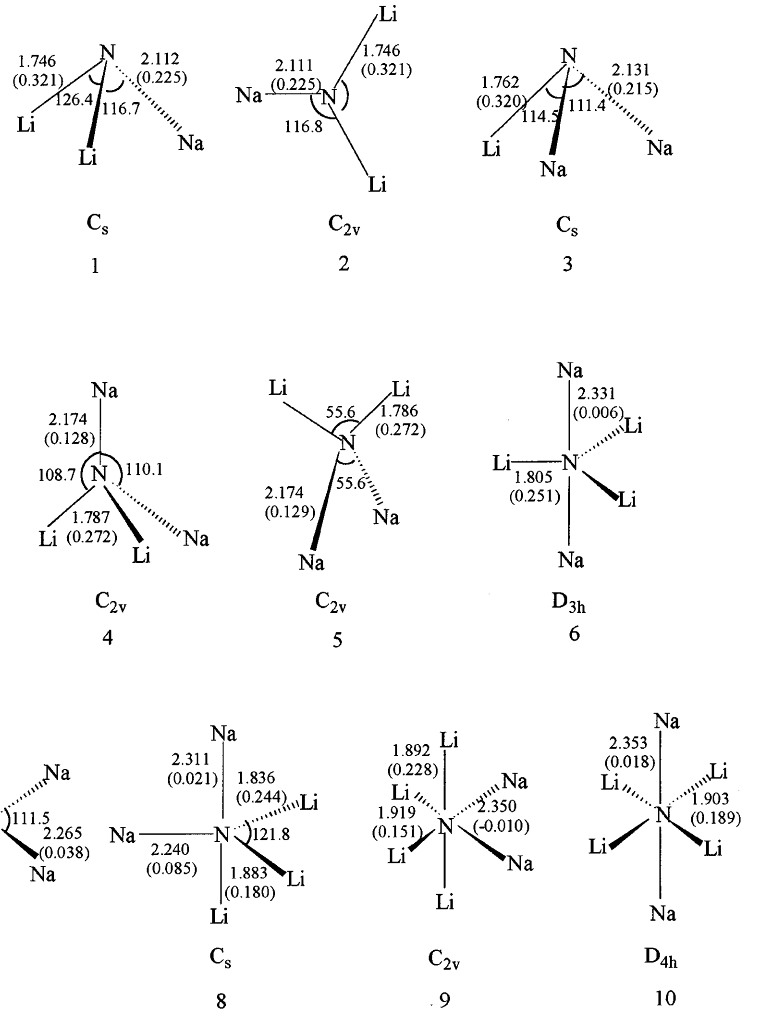

Fig. 1. Optimized geometries and corresponding bond orders of true minima for $NLi_nNa_2(n = 1\text{–}4)$ and NLi_2Na

For the $NLi_3Na_2(D_{3h})$ molecule, the composition of the highest occupied molecular orbital (HOMO) is as follows:

$$\Psi = -0.22S''(N) + 0.60[S''(Na1) + S''(Na2)] - 0.12[S''(Li3) + S''(Li4) + S''(Li5)]$$

Where $S''(A)$ represents the outer orbital for atom A of 6-31G* splitting valence basis; the coefficients of the other atomic orbitals for each atom are much smaller than that listed in this expression. Obviously, the composition of the HOMO for the $NLi_3Na_2(D_{3h})$ species shows a bonding effect with respect to Li-Li as well as N-Li. This can also be seen from the contour map of the HOMO for this molecule in Fig. 2. For coordinated Na atoms, the antibonding property with respect to N-Na and the bonding effect between the two Na atoms are well indicated. It is these interactions between adjacent ligands, Li-Li or Na-Na, that strengthen the stability of these hypervalent species.

3.4 Frequencies

We calculated vibrational frequencies of every species with optimized geometries at the same level. The

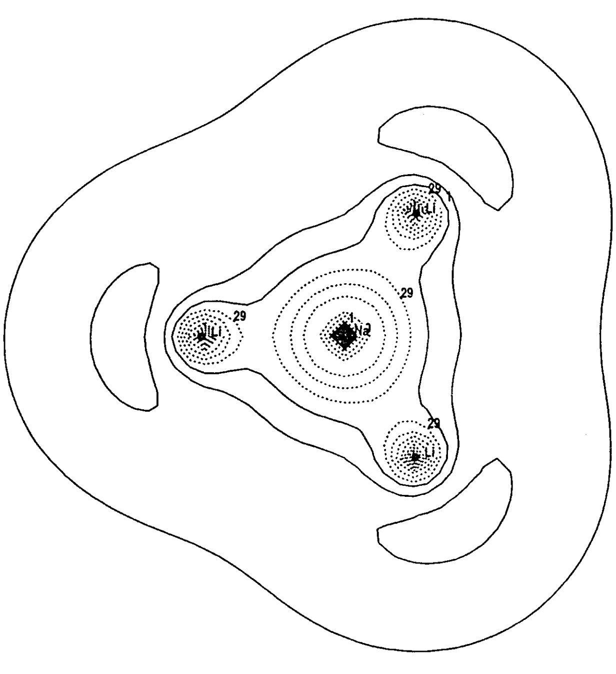

Fig. 2. Contour map of the highest occupied molecular orbital for $NLi_3Na_2(D_{3h})$ species

Table 3. Calculated frequencies of NLi_nNa_2 and NLi_2Na species (cm^{-1}) and corresponding IR intensity (in *parentheses*)

Species	B3LYP/6-31G*// B3LYP/6-31G*	Species	B3LYP/6-31G*// B3LYP/6-31G*
NLi_2Na	a' 20(51)	NLi_3Na_2	e' 87
(C_s)	a'' 153(13)	(D_{3h})	e' 168(45)
	a' 159(6)		a'_1 207
	a' 434(8)		a''_2 221(114)
	a' 769(58)		e'' 229(3)
	a'' 886(67)		a''_2 335(30)
			a'_1 595
			e' 779(1)
$NLiNa_2$	a' 108(25)	NLi_4Na_2	a_1 101(6)
(C_s)	a' 127(27)	(C_{2v})	a_2 106
	a'' 150		b_2 157(1)
	a' 374(3)		a_1 206(169)
	a'' 514(33)		b_2 214(150)
	a' 803(82)		b_1 219(6)
NLi_2Na_2	a_1 84(5)		b_2 246(169)
(C_{2v})	a_2 133(1)		a_1 256
	b_2 134(32)		a_1 297(122)
	b_1 161(3)		a_1 486(9)
	a_1 185(4)		b_2 541(12)
	a_1 352(12)		a_1 562(3)
	b_1 447(33)		b_1 641(28)
	a_1 710(6)		a_2 771
	b_2 788(1)		b_1 1212(109)

calculated values for the global minima of these species are given in Table 3. The values are all positive, which confirms these species to be stationary points on their potential-energy surfaces. Only the low frequency for $NLi_2Na_2(C_{2v})$ is a little small, just 20 cm^{-1}. Up to now there are no experimental data to be compared with our results. The values of our calculations must await experimental tests and will be helpful for experimental studies.

4 Conclusions

We summarize this study as follows.

1. Through geometrical optimizations, we found the most stable configurations to be C_{2v}(NLi_4Na_2, NLi_2Na_2), D_{3h}(NLi_3Na_2) and C_s($NLiNa_2$ and NLi_2Na).
2. Along the series $NLiNa_2$ (NLi_2Na) → NLi_2Na_2 → NLi_3Na_2 → NLi_4Na_2, the bond lengths of N-Li and N-Na increase by about 0.4 Å step by step.
3. For NLi_nNa_2 (n = 1–4), the bond orders between the central N atom and the coordinated Li and Na atoms apparently decrease when the Li atom is gradually added from n = 1. On the other hand, the bond orders of Li-Li and Na-Na increase. The extra electrons (over eight) mainly contribute to the bonding between coordinated atoms.

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