Inverse Sodium Hydride: Density Functional Theory Study of the Large Nonlinear Optical Properties

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“Inverse sodium hydride” ($AdzH^+Na^-$) is an alkalide compound synthesized in recent experiments containing the unusual charge distribution H^+ and Na^- (inverse charge state). The new class of compounds interests scientists to investigate their especial structures and properties. In this paper, the structures of three alkalides compounds, $(Me)_3NH^+Na^-$, $AdzH^+Na^-$, and $AdzLi^+Na^-$, have been obtained in theory. Especially, the structure of $AdzLi^+Na^-$ is still researched by experimental scientists. We investigated the NLO properties of the alkalides complexes for the first time and found that inverse sodium hydride $AdzH^+Na^-$ has a considerably large NLO response $\beta_0 = 5.7675 \times 10^4$ au by density functional theory (DFT). To understand the essential features of the large NLO properties, four related systems have been also calculated. Their first hyperpolarizabilities are $\beta_0 = 7.357 \times 10^3$ au for $(Me)_3NH^+Na^-$, $\beta_0 = 3.9$ au for $(Me)_3NH^+$, $\beta_0 = 1.10 \times 10^2$ au for $(Me)_3NH^+Cl^-$, and $\beta_0 = 6.20681 \times 10^5$ au for $AdzLi^+Na^-$, respectively. By comparing, we found that, first, the Na^- anion plays a crucial role in the considerably large first hyperpolarizability of inverse sodium hydride and, second, the first hyperpolarizability of inverse sodium hydride increases with the charge value of the sodium anion. The above results are useful for designing potential NLO materials.

I. Introduction

During the past twenty years, people have expressed great interest in studying many different types of nonlinear optical (NLO) matters[1−9] to design excellent NLO materials. In our previous work, it is already reported that the species with solvated excess electrons, $(FH)_2\{e\}(HF)$, has the large nonlinear optical (NLO) responses (the first hyperpolarizability $\beta_0 = 8.1 \times 10^7$ au).[10] The loosely bound excess electron is regarded as a decisive factor in the very large first hyperpolarizability of these inorganic NLO matters.

Recently, “electride” and “alkalide” compounds have attracted considerable attention. Electrides[11] are novel materials in which alkali metals ionize to form bound alkali cations and excess electrons.[12] In our previous work, the NLO properties of $(HCN)_nLi$ with electride characteristics have been studied,[13] and its first hyperpolarizability is also considerably large ($\beta_0 \approx 10^4$ au). Alkalides, like electrides, are also reducing materials in which alkali metals replace excess electrons to act as anions (Na^-, K^-, Rb^-, or Cs^-).[14] The excess electron in the anion is loosely bound and may bring the especial optical properties for “alkalides”. At present, the optical absorption and photoelectron emission of some alkalides have been studied,[15,16] but the investigation on the NLO properties has not been reported. We believe that some alkalides containing the loosely bound excess electron should have considerably large NLO responses.

In a recent *J. Am. Chem. Soc.* communication,[17] to explore the synthesis of the room-temperature stable alkalides, the Dye group reported the synthesis and characterization of a crystalline salt in which Na appears as the Na^- alkalide anion and the counterion involves H^+ bound to the 3^6 adamanzane (Adz) hydrocarbon cage (inverse sodium hydride: $AdzH^+Na^-$).[17] Then Simons et al. reported the theoretical study on the stability of inverse sodium hydride using a simple model ($(Me)_3N-H^+ + Na^-$).[18] Investigation suggested that using amines with larger proton affinities and alkali metals with weak M−H bond strengths may allow one to achieve an $R3N-H^+\cdots M^-$ ion pair that is more stable and has a larger barrier to dissociation. It is proved that unprotected protonated amines complexed with alkalides may be synthesized under proper solvent conditions in theory. [18]

The $AdzH^+Na^-$ complex (Figure 1b) is the first hydrogen sodide, in which the proton is stabilized by complexation with four nitrogen atoms of an adamanzane cage. This allows it to survive in the presence of Na^- anions in the solid state and in solution and also with solvated electrons in solution.[17] However, as the Na atom has a small electron affinity (0.54 eV),[19] the excess electron of the Na^- anion gives a loosely bound characteristic. Therefore, we predict the large nonlinear optical properties of the new class of compound with the Na^- anion. Though, to Dye’s mind, the importance of this salt lies in the fact that it challenges the usual NaH solid and enlightens the synthesis of room-temperature stable alkalides, it might also become a new potential class of NLO species.

In this paper, we investigate the considerably large first hyperpolarizabilities of $AdzH^+Na^-$ (synthesized by the Dye group[17]) and prototype $(Me)_3N-H^+ + Na^-$ (designed by the Simons group[18]). It gives a new designing idea for NLO matters and provides a future that alkalides compounds are made into the NLO materials.

II. Methods

The stable structures of three species ($(Me)_3N$, $(Me)_3NH^+$, and $(Me)_3NH^+Na^-$) are obtained at the second-order Møller−Plesset perturbation theory level (MP2) with the aug-cc-pVDZ

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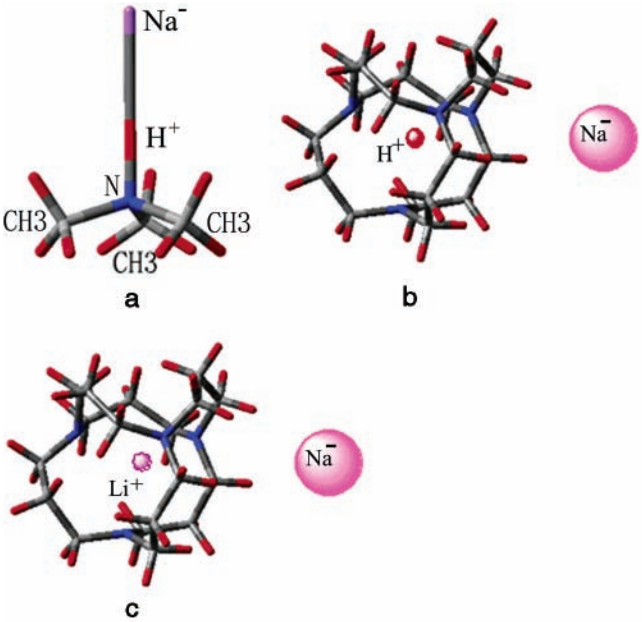

Figure 1. Structures of three species: (a) $(Me)_3NH^+Na^-$; (b) $AdzH^+Na^-$; (c) $AdzLi^+Na^-$. Black denotes C atom, the red denotes H atom, and the blue denotes N atom.

basis set. The structures of $AdzH^+Na^-$ and $AdzLi^+Na^-$ are optimized at the B3LYP/6-31G level.

The first hyperpolarizabilies of three structures ($(Me)_3N$, $(Me)_3NH^+$, and $(Me)_3NH^+Na^-$) also are calculated at the MP2/aug-cc-pVDZ level. The Simons group thinks that Na^- binds its excess electron strongly enough to not require the use of extra diffuse functions.[18] As a result, the extra diffuse functions are not considered in all calculation.

And the first hyperpolarizabilies of $AdzH^+Na^-$ and $AdzLi^+Na^-$ are obtained at the DFT (B3LYP) method. In calculation, we use the 6-31G basis set for the H, C, and N atoms in "Adz" frame and the aug-cc-pVDZ basis set for the Na^- ion and the counterion H^+ or Li^+.

When the system is in the weak and stable applied electric field, its energy can be written as

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma ... \quad (1)$$

where E^0 is the molecular energy without the applied electrostatic field and F_α is a component of the strength on the α direction of applied electrostatic field; μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ may be called a component of dipole, polarizability, and first hyperpolarizability tensor, respectively. The electrostatic properties for the adopted structure are given in terms of components in various directions in the course of calculation. For the sake of having a better illumination for these properties, we analyze the values of μ_0, $\bar{\alpha}$, and β_0. Their expressions are written as follows:

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

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

$$\beta_0 = (\beta_x^{\,2} + \beta_y^{\,2} + \beta_z^{\,2})^{1/2} \quad (4)$$

where

$$\beta_x = \frac{3}{5}(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}) \quad (5)$$

$$\beta_y = \frac{3}{5}(\beta_{yyy} + \beta_{yxx} + \beta_{yzz}) \quad (6)$$

$$\beta_z = \frac{3}{5}(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}) \quad (7)$$

All of calculations performed in this work are carried out using the GAUSSIAN 03 package.[20] Atomic units are used throughout this paper.

III. Results and Discussion

The geometric parameters of three species ($(Me)_3N$, $(Me)_3NH^+$, and $(Me)_3NH^+Na^-$) are obtained at the MP2/aug-cc-pVDZ level and listed in Table 1. All parameters accord with the values by the Simons group.[18] The conformation of $(Me)_3N-H^+ + Na^-$ is shown in Figure 1a. The highest occupied molecular orbital (HOMO) of $(Me)_3NH^+\cdots Na^-$ is pictured in Figure 2a, which shows that the excess electron of Na^- is localized between H atom and Na atom.

A. Suitable Applied Electric Field. The calculational results of the polarizabilities and hyperpolarizabilities rely on an applied electric field (AEF). It is important that the suitable applied electric field is selected to calculate the intrinsic properties of these species containing Na^- anion. In the range 0.0001−0.0030 au, we have tested carefully the suitability of the electric fields at the MP2/aug-cc-pVDZ level. Data for the AEF dependence are displayed in Table 2. The results show that, for $(Me)_3NH^+\cdots Na^-$, there is a plateau for the β_0 value and the vertical ionization energies (VIE) value in an AEF range 0.0001−0.0015 au. From 0.0001 to 0.0015 au AEF, the changes of VIE and the β_0 value are considerably small, only 3.9% for VIE and 3.7% for the β_0 value. It is obvious that the computational results in this AEF range can represent the intrinsic properties of $(Me)_3NH^+\cdots Na^-$. Thus the selected 0.0010 AEF is suitable to be used in the calculations of electric properties for $(Me)_3N$, $(Me)_3NH^+$, $(Me)_3NH^+Na^-$, $(Me)_3NH^+Cl^-$, $AdzH^+Na^-$, and $AdzLi^+Na^-$

B. First Hyperpolarizability of the $(Me)_3N-H^+ + Na^-$ Model. The electric properties of three structures, $(Me)_3N$, $(Me)_3NH^+$, and $(Me)_3NH^+Na^-$, are calculated at the MP2/aug-cc-pVDZ level and given in Table 3. Among the electric properties, the first hyperpolarizability becomes a focus of attention. From Table 3, we find that there are some great differences in the β_0 values for three species. The β_0 value of $(Me)_3N$ is 207.7 au. By attaching the H^+ cation to $(Me)_3N$, the β_0 value decreases obviously to be only 3.9 au for $(Me)_3NH^+$. It is interesting that the first hyperpolarizability dramatically mounts into the 7357.0 au for $(Me)_3NH^+Na^-$ when Na^- is further added on $(Me)_3NH^+$. Obviously, Na^- plays a crucial role in this large first hyperpolarizability of $(Me)_3NH^+Na^-$.

However, does each species of anions have the capacity of bringing the large first hyperpolarizability for the system containing it? To clarify this question, we replace the Na^- anion by the Cl^- anion for $(Me)_3NH^+Na^-$ and model $(Me)_3NH^+Cl^-$ is formed. The structure (Table 1) of $(Me)_3NH^+Cl^-$ is obtained by the partial optimization method (the $(Me)_3NH^+$ frame is frozen) at the MP2/aug-cc-pVDZ level. The electric properties of $(Me)_3NH^+Cl^-$ are also obtained at the MP2/aug-cc-pVDZ level and listed in Table 3. The result shows that its first hyperpolarizability is merely 110.0 au, only one-seventieth of the $(Me)_3NH^+Na^-$ β_0 value. Obviously, it is not true that each

TABLE 1: Bond Lengths (Å) and Angles (deg) for Four Optimized Structures

species	R(C−N)	R(C−H)	R(N−H)	R(Na(Cl)-H)	θ(NCH)	θ(CNC)	θ(CNH)	θ(NHNa)
$(Me)_3N$	1.462	1.101			109.670	109.840		
$(Me)_3NH^+$	1.502	1.097	1.028		108.808	111.312	107.552	
$(Me)_3NH^+Na^-$	1.482	1.100	1.119	2.585	108.143	112.528	106.208	180.0
$(Me)_3NH^+Cl^-$	1.482	1.100	1.119	1.708	108.143	112.528	106.208	

TABLE 2: VIE Values (eV), Dipole Moment, Mean Static Polarizability (au), and First Hyperpolarizability (au) of $(Me)_3NH^+Na^-$ Calculated at MP2/aug-cc-pVDZ Level in Different Applied Electric Fields

field	VIE	μ_0	$\bar{\alpha}$	β_0	$(\beta_0^n - \beta_0^{0.0001})/\beta_0^{0.0001}$
0.0001	3.810	−2.575	307.7	7492.2	0.0%
0.0005	3.851	−2.575	308.3	7439.4	−0.7%
0.0010	3.904	−2.575	308.7	7357.0	−1.8%
0.0015	3.958	−2.575	309.7	7210.8	−3.7%
0.0020	4.013	−2.575	311.3	6990.0	−6.7%
0.0030	4.129	−2.575	315.7	6211.0	−17.1%

species of anions has the capacity of bringing the large first hyperpolarizability for the system containing it.

Why is the β_0 value of $(Me)_3NH^+\cdots Na^-$ much larger than that of the $(Me)_3NH^+Cl^-$? We first consider the two-level model:[21,22]

$$\beta_0 = (3/2)\Delta\mu\cdot f_0/\Delta E^3$$

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. In the two-level expression, the third power of the transition energy is inversely proportional to the β_0 value. So, the transition energy is the decisive factor in the first hyperpolarizability.

The transition energies of two species, $(Me)_3NH^+Na^-$ and $(Me)_3NH^+Cl^-$, are obtained by the TD-DFT method with the aug-cc-pVDZ basis set and listed in Table 4. Table 4 shows that the transition energy of $(Me)_3NH^+Na^-$ is 2.0828 eV and that of $(Me)_3NH^+Cl^-$ is 7.9756 eV. Because the transition energy of $(Me)_3NH^+Na^-$ is much smaller than that of $(Me)_3NH^+Cl^-$, according to the two-level model, it is reasonable that the β_0 value (7357.0 au) of $(Me)_3NH^+Na^-$ is far larger than that (110.0 au) of $(Me)_3NH^+Cl^-$.

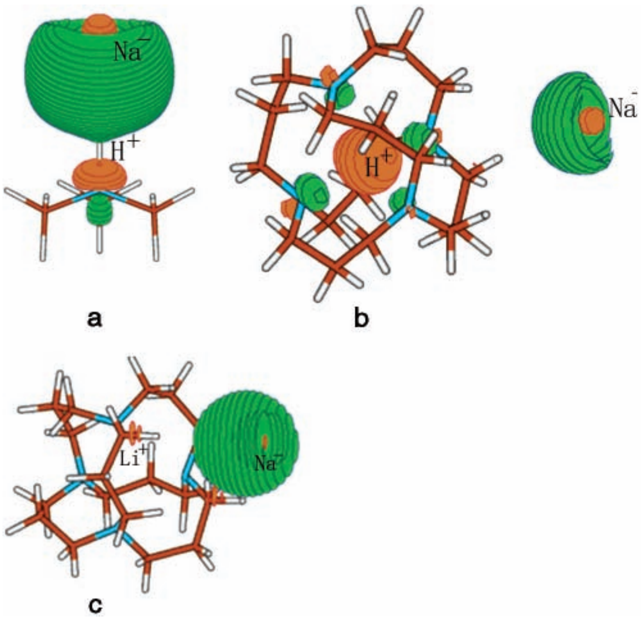

Figure 2. The 0.04 isosurface of the HOMOs for $(Me)_3NH^+Na^-$ (a), $AdzH^+Na^-$ (b), and $AdzLi^+Na^-$ (c). The excess electron is located between H and Na atoms.

From Table 4, the excess electron in HOMO is invoked in crucial transition for $(Me)_3NH^+Na^-$. The atom Na has a quite small electron affinity (0.54 eV).[19] So, for the $Na^- + H^+$ ion pair, such an inverse charge state makes it impossible that the electron from the H atom is seized tightly by the Na atom. As a result, the excess electron in the Na^- anion ought to be loosely bound in space. The HOMO plot (Figure 2a) agrees with this fact. The diffuse nature of this excess electron makes it easily excited, and accordingly, the transition energy in the crucial transition is quite small, $\Delta E = 2.0828$ eV. Differing from the atom Na, the atom Cl has a large electron affinity (3.613 eV).[19] So, in $(Me)_3NH^+Cl^-$, the electron from the H atom is seized by the Cl atom tightly; that is, $(Me)_3NH^+Cl^-$ does not have the excess electron. The transition energy of $(Me)_3NH^+Cl^-$ in the crucial transition is considerably large $\Delta E = 7.9756$ eV. Therefore, the β_0 value of $(Me)_3NH^+Cl^-$ is much smaller than that of $(Me)_3NH^+Na^-$. Hence, it is the essential reason for the large β_0 value that the Na^- anion has the excess electron and the Cl^- anion does not.

C. β_0 Values of $AdzH^+Na^-$ and $AdzLi^+Na^-$. On the basis of the description provided by the Dye group, the structure of the larger system $AdzH^+Na^-$ is optimized at the B3LYP/6-31G level. As shown in Figure 1b, the red ball representing H^+ locates in the center of the Adz cage and the large pink ball representing Na^- locates out of the Adz cage. In the Adz cage, the four $H^+\cdots N$ distances are 2.281, 2.150, 2.280, and 2.150Å, respectively. These distances are larger than the typical H-bond length. For instance, the H-bond length is 1.683 Å in the $NH_3\cdot H_2O$ system[23] and 1.672 Å in the $NH_3\cdot HCl$ system.[24] The four $H^+\cdots N$ distances are almost equal (the largest difference is 0.131 Å). So the proton hopping from one N atom to another N atom is inconspicuous. In addition, the distances between discretional two N atoms are all in the range 3.45−3.90 Å. The calculated R_{HNa} distance is 6.261Å.

Originally, the Dye group had an idea that Li^+ is encapsulated in 3^6 adamanzane to yield $AdzLi^+Na^-$, but now $AdzLi^+Na^-$ is not obtained in experiment. We get the structure of $AdzLi^+Na^-$ at the B3LYP/6-31G theory level. All structural data are displayed in the Supporting Information. The optimized structure of $AdzLi^+Na^-$ is pictured in Figure 1c. Like $AdzH^+Na^-$, the Li^+ cation (small purple ball) is also encapsulated in the center of the 3^6 adamanzane and the Na^- anion (large pink ball) is out of this cage. However, the $Li^+\cdots N$ distances are shortened to be 2.010, 2.003, 2.041 and 2.005Å, respectively. The distances between two discretional N atoms in the Adz cage are also shortened obviously to be in the range of 3.20−3.35 Å compared with $AdzH^+Na^-$. The calculated R_{LiNa} distance is 5.817 Å, 0.48 Å shorter than the R_{HNa} distance.

From Table 4, NBO analysis shows that the charge value of Na^- increases from −0.45 to −0.85 when H^+ is replaced by Li^+. The charge of Li^+ in $AdzLi^+Na^-$ is 0.75, and the corresponding charge of H^+ in $AdzH^+Na^-$ is only 0.17. Thus, the interactions between the Li^+ and other anions (N^- and Na^-) are stronger than those between the H^+ and other anions. These stronger interactions diminish the size of the Adz cage and the R_{LiNa} distance in $AdzLi^+Na^-$. In addition, the energy gap (1.855

TABLE 3: Electric Properties for Six Species (au)

species	$(Me)_3N$	$(Me)_3NH^+$	$(Me)_3NH^+Cl^-$	$(Me)_3NH^+Na^-$	$AdzH^+Na^-$	$AdzLi^+Na^-$
μ_0	0.2710	0.3400	3.4834	2.5748	4.3579	7.7301
$\bar{\alpha}$	51.3	42.7	70.0	289.7	644.3	838.6
β_0	207.7	3.9	110.0	7357.0	57675.0	620681.0

TABLE 4: Parameters of the Crucial Excited State for Four Species by the TD-DFT Method and the NBO Charges of Related Atoms

	$(Me)_3NH^+Cl^-$	$(Me)_3NH^+Na^-$	$AdzH^+Na^-$	$AdzLi^+Na^-$
crucial excited-state composition	HOMO-2 → LUMO HOMO-2 → LUMO+4 HOMO-2 → LUMO+10 HOMO-2 → LUMO+11	HOMO → LUMO+4 HOMO → LUMO+8 HOMO → LUMO+13	HOMO → LUMO+4	HOMO → LUMO+3
transition energy ΔE (eV)	7.9756	2.0828	2.1112	2.1430
oscillator strengths f_0	0.1300	0.3743	0.6506	0.7396
wavelengths (nm)	155	595	587	578
NBO charge of cation		0.11(H^+)	0.17(H^+)	0.75(Li^+)
NBO charge of N atoms		−0.80(N)	−0.58(N2) −0.59(N3) −0.59(N4) −0.58(N5)	−0.60(N2) −0.60(N3) −0.59(N4) −0.60(N5)
NBO charge of Na^-		−0.27	−0.45	−0.85
first hyperpolarizability	110.0	7.357×10^3	5.7675×10^4	6.3083×10^5

eV) between HOMO and LUMO in $AdzLi^+Na^-$ is larger than that in $AdzH^+Na^-$ (0.554 eV). It indicates that the structure $AdzLi^+Na^-$ should be more stable than the structure $AdzH^+Na^-$ to a certain extent. Thus the renewed attempts to synthesize the $AdzLi^+Na^-$ salt should be a valuable work in experiment.

The HOMO plots of $AdzH^+Na^-$ and $AdzLi^+Na^-$ are displayed in Figure 2b,c, respecitively. Obviously, the sodium anion containing the excess electron occupies quite a large space compared with 3^6 adamanzane for $AdzH^+Na^-$ and $AdzLi^+Na^-$. The excess electron presents the significant diffuse nature. The systems with the excess electron have large first hyperpolarizabilities.[10,13] This will predict that $AdzH^+Na^-$ and $AdzLi^+Na^-$ should have the large first hyperpolarizabilities.

The electric properties of $AdzH^+Na^-$ and $AdzLi^+Na^-$ are calculated and listed in Table 3. As expected, the β_0 values of $AdzH^+Na^-$ and $AdzLi^+Na^-$ are quite large, $\beta_0 = 5.7675 \times 10^4$ au for $AdzH^+Na^-$ and 6.20681×10^5 au for $AdzLi^+Na^-$. From section B, it is known that Na^- plays a crucial role in this large first hyperpolarizability.

From Tables 3 and 4, we find that there is an interesting relationship between the β_0 values and the charge values of $Na^-(QNa^-)$ for $(Me)_3NH^+Na^-$, $AdzH^+Na^-$, and $AdzLi^+Na^-$. The system containing Na^- with a larger charge value has the larger first hyperpolarizability. We use the two-level model (containing three factors ΔE, f_0, and $\Delta\mu$) to explain this relationship. Table 4 shows that the ΔE values of $(Me)_3NH^+Na^-$, $AdzH^+Na^-$, and $AdzLi^+Na^-$ are almost equal and the oscillator strengths f_0 of three systems only have small effects on the difference of their β_0 values. Thus the $\Delta\mu$ value should be a key influencing factor in the difference of the β_0 values for $(Me)_3NH^+Na^-$, $AdzH^+Na^-$, and $AdzLi^+Na^-$. We consider that, for three systems, the different charge values of Na^- may significantly affect the $\Delta\mu$ values of three systems, that is, a relationship of $QNa^-((Me)_3NH^+Na^-) < QNa^-(AdzH^+Na^-) < QNa^-(AdzLi^+Na^-)$ is likely to lead to a trend of $\Delta\mu((Me)_3NH^+Na^-) < \Delta\mu(AdzH^+Na^-) < \Delta\mu(AdzLi^+Na^-)$ and finally bring $\beta_0((Me)_3NH^+Na^-) < \beta_0(AdzH^+Na^-) < \beta_0(AdzLi^+Na^-)$.

Thus it can be seen that, for the systems containing the sodium anion, the effective method that increases the first hyperpolarizability is the increase of the charge value of Na^-. We find that two approaches can be used to enhance the charge value of the sodium anion. First, comparison of $(Me)_3NH^+Na^-$ and $AdzH^+Na^-$ shows that the charge value of Na^- has an increase when the Adz cage replaces $(Me)_3N$. Second, comparison of $AdzH^+Na^-$ and $AdzLi^+Na^-$ shows that the charge value of Na^- also has a great increase when the Li^+ cation replaces the H^+ cation. Clearly, the second approach is more effective.

IV. Conclusion

We obtained the structures of three compounds containing the sodium anion in theory, $(Me)_3NH^+Na^-$, $AdzH^+Na^-$, and $AdzLi^+Na^-$. Especially, $AdzLi^+Na^-$ is still desired by the Dye group. The renewed attempts to synthesize the $AdzLi^+Na^-$ salt should be valuable work in experiment on the basis of our work.

The NLO properties are investigated for the first time for alkalide compounds containing the sodium anion. We found that the sodium anion with the excess electron makes the new type of alkalide compounds have a quite large NLO response, $\beta_0 = 7.357 \times 10^3$ au for $(Me)_3NH^+Na^-$, $\beta_0 = 5.7675 \times 10^4$ au for $AdzH^+Na^-$, and $\beta_0 = 6.20681 \times 10^5$ au for $AdzLi^+Na^-$. Comparison of the three compounds shows that the charge value of Na^- has a larger effect on the first hyperpolarizabilities of these compounds. The relationship is that the first hyperpolarizability increases with the charge value of the sodium anion in the three compounds.

We also found that two approaches can be used to enhance the charge value of the sodium anion. First, comparison of $(Me)_3NH^+Na^-$ and $AdzH^+Na^-$ shows that the charge value of Na^- has an increase via the Adz cage replacing the $(Me)_3N$. Second, comparison of $AdzH^+Na^-$ and $AdzLi^+Na^-$ shows that the charge value of Na^- has a further increase when the Li^+ cation replaces the H^+ cation.

The above results from these isolated molecules are useful for giving a new idea to design some potential NLO materials.

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Supporting Information Available: Structures of $AdzH^+Na^-$ and $AdzLi^+Na^-$. The files are available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Eaton, D. F. *Science* **1991**, *253*, 281.

(2) *Nonlinear Optical Properties of Organic Molecules and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1984.

(3) Cheng, W. D.; Xiang, K. H.; Pandey, R.; Pernisz, U. C. *J. Phys. Chem. B* **2000**, *104*, 6737.

(4) Ichida, M.; Sohda, T.; Nakamura, A. *J. Phys. Chem. B* **2000**, *104*, 7082.

(5) Hold, K.; Pawlowski, F.; Jørgensen P.; Hättig, C. *J. Chem. Phys.* **2003**, *118*, 1292.

(6) Hättig, C.; Larsen, H.; Olsen, J.; Jørgensen, P.; Koch, H.; Femández, B.; Rizzo, A. *J. Chem. Phys* **1999**, *111*, 10099.

(7) Horikoshi, R.; Nambu, C.; Mochida, T. *Inorg. Chem.* **2003**, *42*, 6868.

(8) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586.

(9) Shelton, D. P.; Rice, J. E. *Chem. Rev.* **1994**, *94*, 3.

(10) Li, Y.; Li, Z. R.; Wu, D.; Li, R. Y.; Hao, X. Y.; Sun, C. C. *J. Phys. Chem. B* **2004**, *108*, 3145.

(11) Dye, J. L. *Inorg. Chem.* **1997**, *36*, 3816.

(12) Li, Z. Y.; Yang, J. L.; Hou, J. G.; Zhu, Q. S. *J. Am. Chem. Soc.* **2003**, *125*, 6050.

(13) Chen, W.; Li, Z. R.; Wu, D.; Li, R. Y.; Sun, C. C. *J. Phys. Chem. B* **2005**, *109*, 601.

(14) Moloney, D. M. *Nature Genet.* **1996**, *13*, 48.

(15) Hendrickson, J. E.; Pratt, W. P., Jr.; Kuo, C. T.; Xie, Q. S.; Dye, J. L. *J. Phys. Chem.* **1996**, *100*, 3395.

(16) Kuo, C. T.; Dye, J. L. *J. Phys. Chem.* **1994**, *98*, 13575.

(17) Redko, M. Y.; Vlassa, M.; Jackson, J. E.; Misiolek, A. W.; Huang, R. H.; Dye, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 5928.

(18) Sawicka, A.; Skurski, P.; Simons, J. *J. Am. Chem. Soc.* **2003**, *125*, 3954.

(19) *Atoms and Molecules: An Introduction For Students of Physical Chemistry*, Karplus, Martin; Porter, Richard N.. Eds.; The Benjamin/Cummings Publishing Co.: Menlo Park, CaA, Reading, MA, London, Amsterdam, Don Mills, Ontario, Sydney, 1970.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(21) Kanls, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195.

(22) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446.

(23) Fortes, A. D.; Brodholt, J. P.; Wood, I. G.; Vočadlo, L.; Jenkins H. D. B. *J. Chem. Phys.* **2001**, *115*, 7006.

(24) Li, R. J.; Li, Z. R.; Wu, D.; Hao, X. Y.; Li, Y.; Wang, B. Q.; Tao, F. M.; Sun, C. C. *Chem. Phys. Lett.* **2003**, *372*, 893.