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Thermodynamic stability and optimized structures of hypervalent molecules M_2CN ($M = Li, Na, K$)

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Abstract

The hypervalent M_2CN ($M = Li, Na, K$) molecules have been detected in the vapor at elevated temperatures over mixtures of alkali metals and sodium cyanide by means of Knudsen-effusion mass spectrometry. The experimentally obtained ionization energies were IP (Li_2CN^+) $= 5.4 \pm 0.2$ eV, IP(Na_2CN^+) $= 4.9 \pm 0.2$ eV and IP (K_2CN^+) $= 4.0 \pm 0.2$ eV, agreeing well with the theoretical values 5.13, 4.66 and 3.7 eV, respectively, calculated for the vertical ionization. The energies of dissociation into MCN and M were D_0° (LiNC–Li) $= 137 \pm 14$ kJ/mol, D_0° (NaCN–Na) $= 104 \pm 14$ kJ/mol, and D_0° (KCN–K) $= 81 \pm 8$ kJ/mol. Although the theoretically calculated values were slightly lower (103.8 kJ/mol for Li_2CN, 72.8 kJ/mol for Na_2CN, and 74.5 kJ/mol for K_2CN), the dissociation energies indicate moderately strong bonding of alkali metals to the alkali cyanides (MCN) of octet molecules. The agreement between experiment and theory confirms the existence of the M_2CN species, which are the hypervalent molecules with more than one electronegative atom. The theoretically optimized structures of M_2CN are quite similar to each other, with four isomers (two planar structures with C_s symmetry and two linear structure with $C_{\infty v}$ symmetry), although there are differences in bond length. The favored structure of M_2CN has C_s symmetry and is best described as a complex of the CN^- anion with the M_2^+ cation.

Keywords: ab initio MO calculations; Hypervalent molecules; Mass spectrometry; Molecular structures; Thermochemistry

1. Introduction

The study of the nature of bonding in hypervalent molecules is a subject of continuing interest. Experiments as well as theoretical calculations have provided evidence that hyperlithiated molecules such as Li_3O, Li_3S, and Li_4P with 9 valence electrons and CLi_6, Li_4O, and Li_4S with 10 valence electrons are thermodynamically stable, despite their unusual stoichiometries [1–31]. The stability of these molecules is ascribed to the Li–Li bond between all pairs of lithium atoms or 'cage' formation arising from excessive valence electrons. The overall features can be described in terms of a negatively charged center A^{m-}; $A = C, O, P, S$) embedded in a positively charged lithium cage or cluster (Li_n^{m+}).

In our previous papers [32–34], we have reported an experimental characterization as well as a theoretical study of the thermodynamic stability of another type of hyperlithiated species, Li_2CN, with more than one electronegative atom. The molecule exhibited a complex potential energy surface with several minima of comparable stability. The results of geometry optimization indicated that the two lowest energy structures of Li_2CN had C_s symmetry; both isomers were best

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described as complexes of CN^- with Li_2^+ radical cation.

In extended experiments with Knudsen-effusion mass spectrometry, we have recently detected similar molecules Na_2CN and K_2CN composed of other alkali metals. This paper discusses the stability and structures of these hypervalent molecules M_2CN (M = Li, Na, K), based on their thermochemical properties obtained by experiments as well as ab initio calculations.

2. Theoretical calculations

The bond dissociation energy (D_0°) and ionization energy (IP) of Li_2CN, Na_2CN, and K_2CN were computed ab initio using a quadratic configuration interaction theory, including triple and quadrupole substitutions (QCISD(T)), the multireference single- and double-excitation configuration interaction method (MRCI) [35], as well as a density functional theory (DFT) [36] using both the local density approximation (LDA) and non-local corrections (NL). The details of the theoretical calculation have been described elsewhere [33].

Reference wavefunctions were obtained from complete active space (CAS) self-consistent (SCF) procedures. All configurations with an absolute CI coefficient $|c_i|$ greater than 0.05 were used as the reference configurations in the subsequent MRCI calculations. Total energies were taken from estimated full CI energies with Davidson's correction [37]. The MRCI calculations were carried out using MOLCAS2 [38].

Geometry optimizations, performed with the Gaussian92 program [39] at the MP2(FU)/6-31 + G* level, located the M_2CN (M = Li, Na, K) minima. Table 1 lists the geometric parameters and vibrational frequencies of each of the four isomers of M_2CN molecules: two non-linear planar structures with C_s symmetry and two linear structures with $C_{\infty v}$ symmetry.

Vertical ionization energies were calculated as the MRCI total energy of the neutral molecule relative to the singly charged molecular ions at the geometry of the neutral. The bond dissociation energies of M_2CN to liberate one M atom, D_0° (MCN–M), were calculated as the MRCI energy of M_2CN relative to a supermolecule, MCN + M, separated by 30 Å. The vibrational correction was accounted for using MP2(FU)/6-31 + G* frequencies.

3. Experimental

Thermochemical properties of gaseous M_2CN (M = Li, Na, K) species were obtained by means of a specially designed Knudsen-effusion mass spectrometer illustrated in Fig. 1. The apparatus consists of a cross-beam ionizer, a quadrupole mass filter, and an electron multiplier with a conversion dynode, all of which are installed in an ultrahigh vacuum (UHV)

Table 1
Vibrational frequencies of gaseous M_2CN (M = Li, Na, K) molecules calculated at the MP2(FU)/6-31 + G* level

Molecule	Point group	ZPE [a]	Frequency/cm^{-1}
Li_2CN 1	C_s	22.3	191, 220, 247, 337, 501, 2123
Li_2CN 2	C_s	21.2	154, 164, 273, 410, 521, 2029
Li_2CN 3	$C_{\infty v}$	22.3	78(2), 217(2), 410, 597, 2142
Li_2CN 4	$C_{\infty v}$	22.1	72(2), 204(2), 373, 656, 2111
Na_2CN 5	C_s	17.8	126, 140, 151, 242, 305, 2021
Na_2CN 6	C_s	18.1	123, 136, 157, 251, 302, 2072
Na_2CN 7	$C_{\infty v}$	20.2	81(2), 212, 253(2), 391, 2116
Na_2CN 8	$C_{\infty v}$	19.4	72(2), 167, 218(2), 416, 2091
K_2CN 9	C_s	16.3	74, 93, 96, 209, 223, 2031
K_2CN 10	C_s	15.9	72, 79, 103, 171, 200, 2024
K_2CN 11	$C_{\infty v}$	16.1	20(2), 103(2), 123, 260, 2056
K_2CN 12	$C_{\infty v}$	16.2	3(2), 94(2), 117, 271, 2055

[a] Zero-point vibrational energy in kJ/mol.

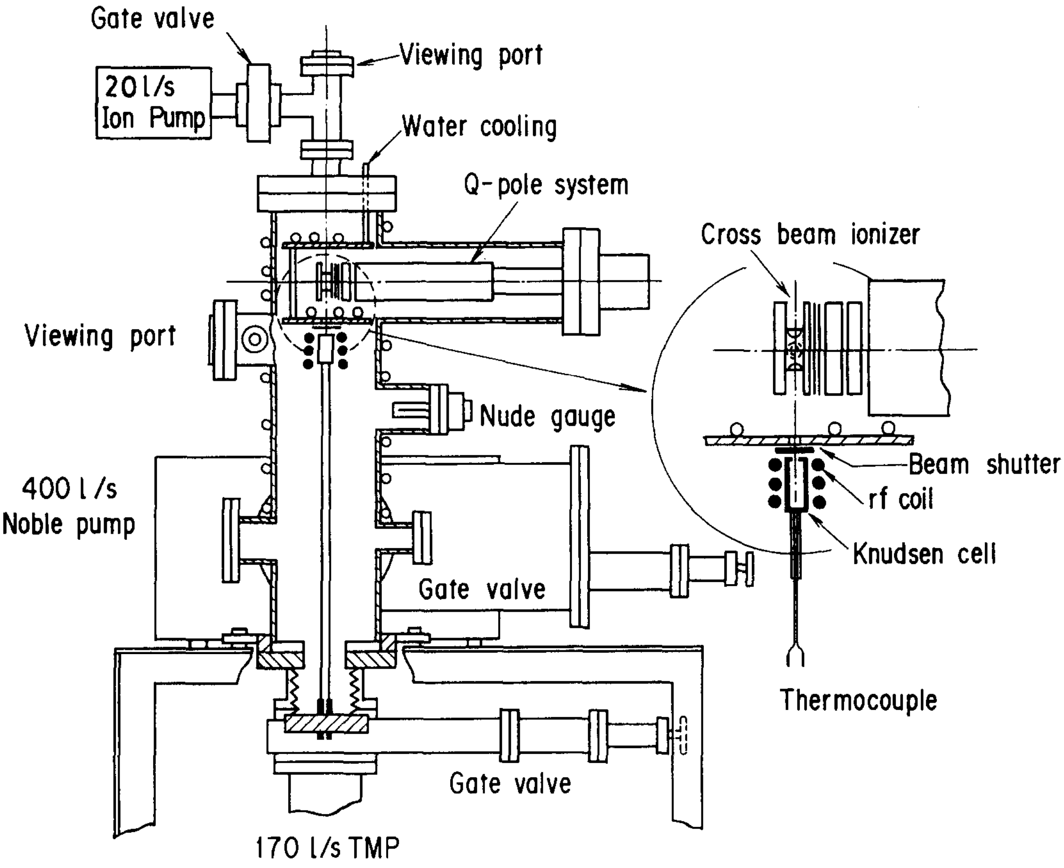

Fig. 1. A sketch of a specially designed Knudsen-effusion mass spectrometer installed in UHV system.

chamber. The background pressure of the UHV system was kept below 6×10^{-7} Pa at room temperature and 4×10^{-5} Pa during the measurements at elevated temperatures. A mixture of alkali metals and NaCN was loaded in a molybdenum Knudsen cell and heated by a radiofrequency generator. The cell temperature, controlled within ±5 K at 1000 K, was measured with both a thermocouple (R-type) embedded at the bottom of the cell and an optical pyrometer, which were calibrated in situ at the triple points of Al and Ag. The volume of the Knudsen cell was 1.5 cm^3 and the orifice diameter was 0.3 mm. Molecular species effusing from the cell were directly introduced into the ionizer. A shutter was inserted between the cell and the ionizer to discriminate the molecular beam from the residual gas; molecular species in the beam were analyzed by the mass spectrometer only when the shutter was open.

The effusing gaseous species were ionized by electron impact at the energy around 5 eV higher than the ionization energy of molecules to be detected. Identification of the species was achieved from their mass-to-charge ratio, appearance energy, isotopic abundance and shutterability. The partial pressure p_i of the species i was determined in the usual manner [40], based on the relation

$$p_i = \kappa(I_i T/\sigma_i \beta_i \gamma_i), \qquad (1)$$

where κ is the proportionality constant, I_i the ion intensity, σ_i the relative ionization cross section, β_i the isotopic abundance and γ_i the multiplier gain of the detector. The proportionality constant κ was obtained from comparison of the observed I_{Li}-to-$I_{\mathrm{Li_2}}$ ratio with the equilibrium constant reported for the $\mathrm{Li_2(g)} = \mathrm{2Li(g)}$ reaction [41]. The molecular ionization cross-section was calculated by taking the sum of

Mann's cross-sections [42]. The multiplier gain of the detector was obtained from a calibration curve.

4. Results and discussion

Substituting the observed signal intensities of mass spectra for I_i in Eq. (1), one can obtain the equilibrium partial pressures of molecules in the cell. Fig. 2 illustrates the partial pressures of Na(g), Na_2(g), Na_3(g), Na_2CN(g), NaCN(g), K(g), KCN(g), K_2CN(g) and K_2(g) in the equilibrium vapor over a mixture of alkali metals and NaCN as a function of the reciprocal temperature; the equilibrium partial pressures of Li(g), Li_2(g), LiNC(g), Li_2CN(g) and Li_3(g) were reported in a previous paper [32]. From the equilibrium constant K_p evaluated from the partial pressures and the thermodynamic relation

$$-\Delta H^\circ_{298}/T = R\ln K_p + \Delta[(G^\circ_T - H^\circ_{298})/T], \tag{2}$$

the enthalpies of Reactions (3–5)

$$Li_2CN(g) \rightarrow LiNC(g) + Li(g) \tag{3}$$

$$Na_2CN(g) \rightarrow NaCN(g) + Na(g) \tag{4}$$

$$K_2CN(g) \rightarrow KCN(g) + K(g) \tag{5}$$

were determined as $\Delta H^\circ_0 = 136.8 \pm 13.8$ kJ/mol; $\Delta H^\circ_0 = 104.6 \pm 3.3$ kJ/mol, and $\Delta H^\circ_0 = 84.5 \pm 21.8$ kJ/mol. Here, it should be noted that the dissociation product of Li_2CN is different from that of Na_2CN and K_2CN; the former gives the isocyanide while the latter two give cyanides [32]. The free energy functions, $\Delta[(G^\circ_T - H^\circ_{298})/T]$, of Li(g), Li_2(g), Na(g), Na_2(g), K(g), K_2(g), NaCN(g) and

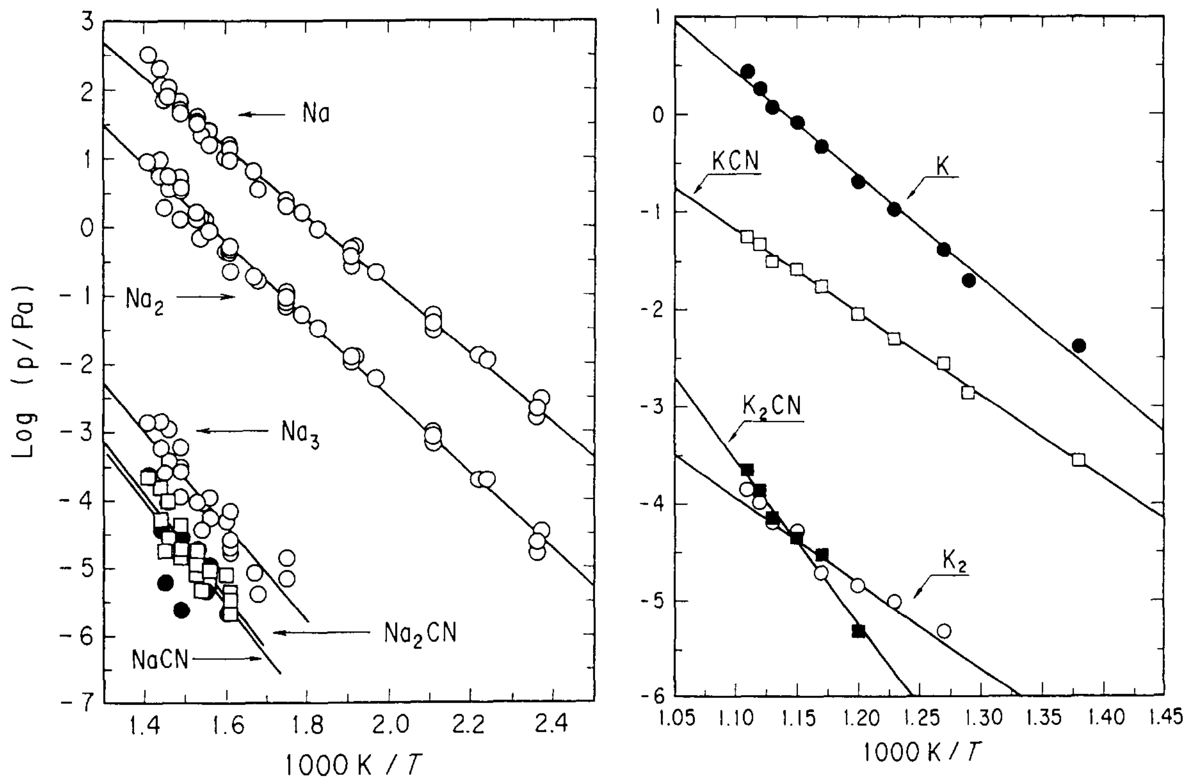

Fig. 2. Equilibrium vapor pressures of gaseous species over a mixture of Na or K and NaCN as a function of reciprocal of temperatures; the left graph is for a mixture of Na and NaCN and the right graph is for a mixture of K and NaCN. The pressures for the Li and NaCN mixture were reported in Ref. [32].

Table 2
Free energy functions $-(G^\circ_T - H^\circ_{298})/T$ and heat content $(H^\circ_T - H^\circ_{298})$ for gaseous LiNC and M_2CN (M = Li, Na, K) molecules calculated by a statistical thermodynamical method

T/K	$-(G^\circ_T - H^\circ_{298})/T$ in J mol^{-1} K^{-1}		$(H^\circ_T - H^\circ_{298})$ in kJ mol^{-1}	
	LiNC(g)	$Li_2Cn(g)$	LiNC(g)	Li_2CN
0	infinite	infinite	-12.21	-15.30
298.15	238.00	286.08	0	0
400	239.77	288.76	4.62	6.97
500	243.14	293.88	9.21	14.09
600	246.93	299.72	13.87	21.39
700	250.77	305.65	18.61	28.84
800	256.50	311.45	23.43	36.41
		$Na_2CN(g)$		$Na_2CN(g)$
0		infinite		-17.53
298.15		330.82		0
400		333.66		7.39
500		339.06		14.79
600		345.17		22.29
700		351.33		29.90
800		357.32		37.60
		$K_2CN(g)$		$K_2CN(g)$
0		infinite		-18.71
298.15		344.43		0
400		347.31		7.50
500		352.90		14.95
600		358.95		22.50
700		365.18		30.13
800		371.20		37.85

The molecular parameters are listed in Table 1.

KCN(g) were taken from JANAF Tables [43], while those of LiNC(g), $Li_2CN(g)$, $Na_2CN(g)$ and $K_2CN(g)$ were calculated by a statistical thermodynamical method using the molecular parameters listed in Table 1. The free energy functions of LiNC(g), $Li_2CN(g)$, $Na_2CN(g)$ and $K_2CN(g)$ are given in Table 2.

The theoretically calculated bond dissociation energies of M_2CN to liberate one M atom, D°_0 (MCN–M), are 103.8 kJ/mol for Li_2CN, 72.8 kJ/mol for Na_2CN, and 84.5 kJ/mol for K_2CN as summarized in Table 3. This table also lists the observed ionization energies for $Li_2CN(g)$, $Na_2CN(g)$ and $K_2CN(g)$, which were evaluated by the extrapolated voltage difference method [44] with the ionization energies of $IP(Li^+) = 5.392\,eV$, $IP(Li_2^+) = 4.86\,eV$, $IP(Na^+) = 5.139\,eV$, $IP(Na_2^+) = 4.889\,eV$, $IP(K^+) = 4.36\,eV$, and $IP(K_2^+) = 4.06\,eV$ taken as references [45]. The experimental values of $IP(LiNC^+) = 9.24 \pm 0.20\,eV$, $IP(Li_2CN^+) = 5.39 \pm 0.20\,eV$, $IP(NaCN^+) = 8.70 \pm 0.20\,eV$, $IP(Na_2CN^+) = 4.92 \pm 0.20\,eV$, $IP(K_2CN^+) = 4.5 \pm 0.5\,eV$ agreed well with theoretically calculated vertical ionization energies.

Fig. 3 shows the molecular structures of M_2CN obtained by theoretical calculations. Computational geometry optimization at MP2(FC)/6-31G* and MP2(FU)/6-31 + G* gives four possible isomeric structures to the Li_2CN molecule; that is, the planar structures 1 and 2 with C_s symmetry and the linear structures 3 and 4 with $C_{\infty v}$ symmetry. The latter two isomers are 'electronomers' [46,47]. All the isomers have a short C–N bond length (ca 1.19 Å), indicative of a triple bond between C and N. The calculated Wiberg bond index also indicates triple-bond or near-triple-bond character for 1–4. This implies that Li_2CN is a hypervalent molecule, LiNC with an 'extra' Li

Table 3
Dissociation energies (D_0°), ionization energies (IP) and M–M bond lengths (r_{M-M}) of gaseous M_2 and M_2^+ species

Species	D_0° (MCN–M)/(kJ/mol)		IP/eV		r_{M-M}/Å
	Theor. [a]	Expt.	Theor. [a]	Expt.	Theor. [a]
Li_2		106.7±2.5			2.777
Li_2^+		158.2		4.86	3.160
Li_2CN	103.8	136.8±13.8	5.13	5.39±0.2	2.899
Na_2		75.7			3.152
Na_2^+		100.0		4.89	3.653
Na_2CN	72.8	104.6±3.4	4.66	4.92±0.2	3.276
K_2		49.8±1.3			4.206
K_2^+		76.1		4.06	4.856
K_2CN	72.0	84.5±21.8	3.70	4.50±0.5	4.011

[a] MRCI calculation.

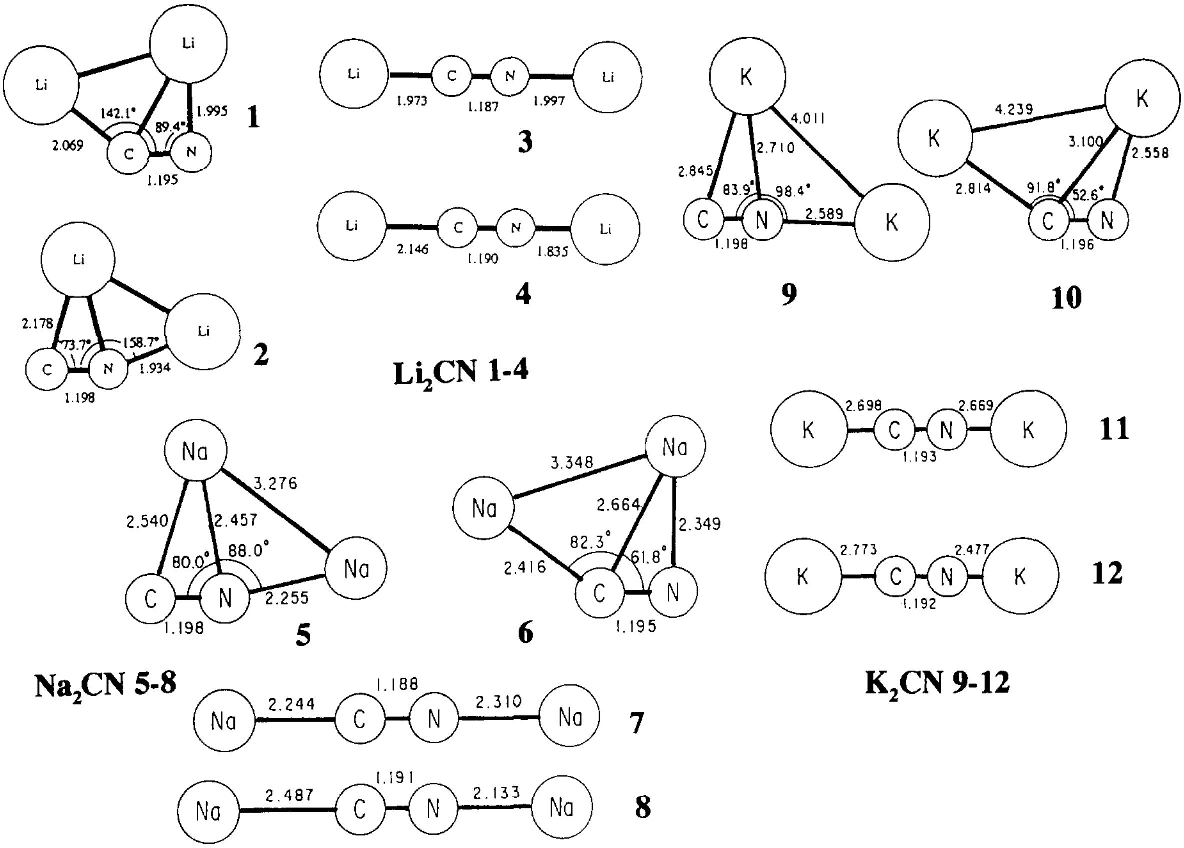

Fig. 3. Equilibrium geometries of Li_2CN 1–4 optimized at MP2(FC)/6-31G* and those of Na_2CN 5–8 and K_2CN 9–12 optimized at MP2(FU)/6-31 + G* (bond distances in angstroms).

atom. The global minimum is 1, although 2 is only 0.8 kJ/mol less stable at QCISD(T)(FC)/6-31 + G*//MP2(FU)/6-31 + G*. At this level, structures 3 and 4 are 40 and 37 kJ/mol higher in energy than 1, respectively. MRCI calculations give a similar picture; 1 and 2 have almost the same energy, with 2 being favored by 0.04 kJ/mol and with 3 and 4 being 36 and 50 kJ/mol less stable than 1, respectively. Density functional calculation (BLYP/6-31G(2df) also favor 1 (0.8 kJ/mol) over 2, with both 3 and 4 being about 40 kJ/mol higher in energy than 1. Thus, only the planar isomers 1 and 2 with C_s symmetry are stable structures.

The same is true for both the Na_2CN and K_2CN molecules. For Na_2CN, the planar structure 5 is the global minimum at the MP2(FC)/6-31 + G* level. The planar structure 6 is nearly as stable as 5, and the calculated total energy of 6 is actually 0.4 kJ/mol lower than that of 5 at the MRCI level. At the B3LYP/6-311 + G* level, the total energy of 6 is 1.1 kJ/mol higher than that of 5. Hence, there are no distinguishable differences in potential energy between the structures 5 and 6. Also in the K_2CN system, the planar structures 9 and 10 are more stable than the linear structures 11 and 12. At the MP2(FU)/6-31 + G* level, the most stable structure is 9, while 10 is more stable than 9 at the MRCI level. The energy difference between these two isomers is only 1.9 kJ/mol at the MRCI level. The most stable structure is dependent on the level of calculations for the geometry optimization. There are no distinguishable differences in the thermodynamical stability between 9 and 10.

The valence molecular orbitals of Li_2CN (1, 2) with C_s symmetry are described as $(5a')^2(6a')^2(7a')^2(1a'')^2(8a')^2(9a')^1$. The 9a′ singly occupied orbital (SOMO) corresponds to the Li_2^+ radical cation MO and contributes to Li–Li bonding, as shown in Fig. 4. The other electrons are distributed around the CN moiety. The in-plane valence electron density of 1 and 2 reveals the interaction between the Li_2^+ and CN^- units, and the planar Li_2CN molecules can both be described as complexes of a cyanide anion with a Li_2^+ radical cation. This description is confirmed both by the short Li–Li distance of about 2.6 Å, which is very similar to that calculated for Li_2^+ (2.63 Å at MP2/6-31G*), and by the natural charge of about +0.5 on each lithium center in 1 and 2. Thus, Li_2CN is an example of a species in which a charged Li_n^{m+} fragment (here Li_2^+) is present. The existence of such transferable charged fragments in perlithiated and hyperlithiated species has recently been pointed out by Schleyer's analysis of C_2Li_6 and C_2Li_4 [48] and extensions of Marsden's work on CLi_8 and CLi_{12} [18].

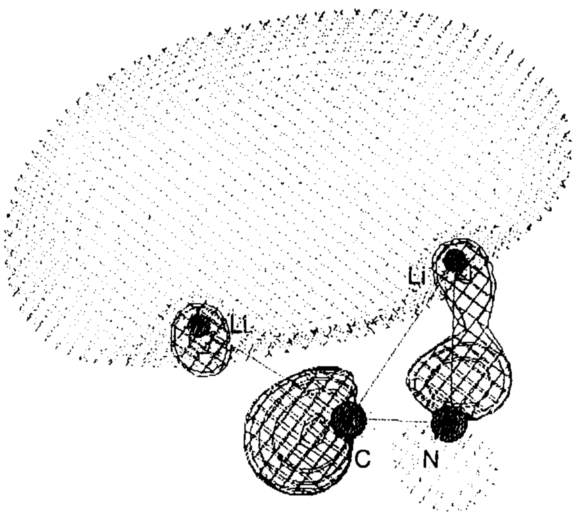

Fig. 4. Feature of singly occupied molecular orbital (SOMO) in Li_2CN 1 with C_s symmetry deduced from MP2(FC)/6-31G* calculations.

This explanation is also possible for the bonding in Na_2CN and K_2CN molecules with C_s symmetry, the valence molecular orbitals of which are described as $(11a')^2(12a')^2(13a')^2(2a'')^2(14a')^2(15a')^1$ and $(17a')^2(18a')^2(19a')^2(3a'')^2(20a')^2(21a')^1$, respectively.

The valence molecular orbitals of Li_2CN (3, 4) with $C_{\infty v}$ symmetry are described as $(3\sigma)^2(4\sigma)^2(2\pi)^4(5\sigma)^2(6\sigma)^1$ and an extra electron is localized on either of the Li atoms. The linear LiCNLi structure 3 is a minimum, but 3 is 40 kJ/mol higher in energy than 1. The extra valence electron in SOMO of 3 is localized on the Li atom near the N atom. On the other hand, the extra valence electron of 4 is localized on the Li atom near C atom. Hence, these 'electronomers' [46,47] can be described as $Li^+(CN)^-Li\cdot$ (3) and $Li\cdot(CN)^-Li^+$(4). The similar energies of 3 and 4 reflect the comparable stabilities of LiCN and LiNC.

The valence molecular orbitals of the linear isomers (7, 8) with $C_{\infty v}$ symmetry are $(9\sigma)^2(10\sigma)^2(3\pi)^4(11\sigma)^2(12\sigma)^1$ and the extra valence electron is localized on either of the Na atoms. The linear NaCNNa structure 7 is a minimum, but 7 is 49 kJ/mol higher in energy than 5. The extra valence electron of 7 is localized on the Na atom near the N atom. The energy of 8 is 50 kJ/mol higher than that of 5. The extra valence electron of 8 is localized on the Na atom near the C atom. Hence, these "electronomers" can be described as $Na^+(CN)^-$ Na·(7) and Na·$(CN)^-Na^+$(8).

The valence molecular orbitals of K_2CN with $C_{\infty v}$ symmetry are described as $(15\sigma)^2(16\sigma)^2(4\pi)^4(17\sigma)^2(18\sigma)^1$ and the extra valence electron is localized on either of the K atoms. The linear structure 11 is 27.5 kJ/mol higher in energy than 9. The extra valence electron of 11 localizes around the K atom near the C atom. The potential energy of 12 is 29.8 kJ/mol higher than that of 9. The extra electron of 12 localizes around the K atom close to the N atom. The linear isomers of K_2CN are described as $K^+(CN)^-$K·(11) and K·$(CN)^-K^+$ (12).

As shown in Table 3, the observed dissociation energy of Na_2CN, D_0° (NaCN–Na) = 104.6 ± 3.3 kJ/mol, was somewhat lower than that of Li_2CN, D_0° (LiNC–Li) = 136.8 ± 13.8 kJ/mol. The dissociation energy of K_2CN, D_0° (KiCN–K) = 84.5 ± 21.8 kJ/mol, was 52.3 ± 7.9 kJ/mol smaller than that of Li_2CN. The difference in experimental dissociation energies for metal atom loss between Na_2CN and Li_2CN is 33.1 ± 10.9 kJ/mol. The difference in the theoretical values is 31.0 kJ/mol at the MRCI level. This value coincides with 32.3 ± 2.5 kJ/mol[14] of the difference in the atomization energies between the Na_2 and Li_2 molecules.

The dissociation of M_2CN molecules to give M and MCN would be associated with the dissociation of M_2^+ radical cations. In this respect, it is interesting to compare the M–M bond length or bond strength of M_2^+ species. The MP2(FU)/6-31 + G* Li–Li bond length (2.899 Å) in Li_2CN is shorter than in the Li_2^+ cation (3.160 Å) but slightly longer than in the Li_2 molecules (2.777 Å). The Na–Na bond length (3.276 Å) in Na_2CN is shorter than that in the Na_2^+ cation (3.653 Å) but longer than in the Na_2 molecule (3.152 Å). The K–K bond length (4.011 Å) in K_2CN is shorter than in the K_2^+ cation (4.856 Å) and also shorter than in the K_2 molecule (4.206 Å).

5. Conclusion

The existence of hypervalent molecules like Li_2CN, Na_2CN, and K_2CN has been demonstrated by mass spectrometric observations as well as ab initio calculations. Of these species, Li_2CN is the most stable toward dissociation; that is, the dissociation energies determined are D_0° (LiNC–Li) = 137 ± 14 kJ/mol, D_0°(NaCN–Na) = 104 ± 13 kJ/mol, and D_0°(KCN–K) = 85 ± 15 kJ/mol. Theoretical calculations indicate that these species would be composed of the M_2^+ (M = Li, Na, K) radical cation and the CN^- anion. The short C–N bond length (ca. 1.19 Å) is indicative of a triple bond between C and N. The presence of the M_2^+ unit justifies the term *hypervalent* for these systems. The extra valence electron in SOMO corresponds to the M_2^+ radical cation, and contributes to M–M bonding. In addition, these molecules are revealed to have four stable isomers slightly different in energy; the planar structures are more stable than the linear structures. The linear structures of M_2CN are electronomers and best described as complexes like $M^+(CN)^-$M· and M·$(CN)^-M^+$.

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