Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 227 (2003) 391–399

www.elsevier.com/locate/ijms

Thermochemical stabilities of the gas-phase cluster ions $H_3C^+(N_2)_n$

Kenzo Hiraoka[a,*], Kiyotoshi Takao[a], Fumiyuki Nakagawa[a], Tomoyuki Iino[a], Masayumi Ishida[a], Kazuo Fujita[a], Koki Hiizumi[a], Shinichi Yamabe[b]

[a] *Clean Energy Research Center, Yamanashi University, Takeda-4, Kofu 400-8511, Japan*
[b] *Department of Chemistry, Nara University of Education, Nara 630-8528, Japan*

Received 12 February 2002; accepted 11 June 2002

Abstract

Gas-phase equilibria for clustering reactions of CH_3^+ with N_2 were measured with a pulsed electron-beam high-pressure mass spectrometer. The bond energies were found to show irregular decreases for $H_3C^+(N_2)_n$ with $n = 1$, 4, and 6. Due to the formation of the covalent bond with $n = 1$, the positive charge is dispersed in the $H_3CN_2^+$ complex which is solvated preferentially by three more N_2 ligands. The ab initio calculations revealed that the cluster ion with $n = 4$ has the three-fold shell structure, $H_3CN_2^+(N_2)_3$, with the C_{3v} symmetry. The most stable cluster ion with $n = 6$ has the four-fold shell structure $(N_2)_1H_3CN_2^+(N_2)_4$. The attachment of $n = 7$ and 8 N_2 ligands results in the relaxation of the four-fold structure of the cluster with $n = 6$ to the three-fold one with $n = 8$, $(N_2)_1H_3CN_2^+(N_2)_3(N_2)_3$, due to the steric congestion.

Keywords: Gas-phase equilibria; Cluster ion; High pressure mass spectrometer

1. Introduction

Methyl cation is a strong Lewis acid and can be bound to neutral molecules with large bond energies. For instance, the bond energies for H_3C^+–CO and H_3C^+–H_2 are 78.9 [1] and 45.3 kcal/mol [2], respectively. A rare gas Ar can be linked with CH_3^+ with the bond energy of 11.3 kcal/mol [3]. Strong coordinations of the first neutral molecules make cation characters delocalized. Therefore, coordinations of more neutral molecules are generally weak. For instance, the $H_3C^+CO \cdots CO$ energy is only 4.5 kcal/mol [1].

In spite of accumulation of many thermochemical data of gas-phase clustering reactions, a combination of the methyl cation and nitrogen molecules, although fundamental, has not been investigated so far except for $n = 1$ [4–6].

$$H_3C^+(N_2)_{n-1} + N_2 = H_3C^+(N_2)_n \qquad (1)$$

Since N_2 is less nucleophilic than CO, smaller bond energies in reaction (1) than those for CO are expected. Careful low temperature measurements would be required for the determination of the bond energies with $n \geq 2$. In the $H_3C^+(CO)_n$ cluster, only the species of $n \leq 7$ have been detected [1]. Due to the truncation, an insight into the saturation shell could not be obtained for CO. It is a challenge whether the insight can

---

* Corresponding author. Tel.: +81-522-20-8572; fax: +81-522-20-8572.
E-mail address: hiraoka@ab11.yamanashi.ac.jp (K. Hiraoka).

1387-3806/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00097-6

be derived from the study of reaction (1). In fact, the inner shell completion has been suggested here with $n = 6$ for N_2 in reaction (1).

In order to evaluate small bond energies, accurate and high quality theoretical calculations are necessary. But, so far, these calculations (e.g., QCISD(T), CCSD) have been difficult for large-size clusters. Recent progress of density-functional theory (DFT) calculations has changed the situations drastically [7]. DFT ones are now deemed standard methods to evaluate energies and structures practically and reliably. It is of theoretical interest to check whether DFT calculations may reproduce small (a few kcal/mol) bond energies of reaction (1) satisfactorily. Thus, the insight is tackled by an experiment–calculation combination study.

2. Experimental and computational methods

The experiments were made with a pulsed electron-beam high-pressure mass spectrometer [8,9]. The major gas N_2 at a few torr was purified by passing it through a dry-ice acetone cooled 5A molecular sieve trap. A few microtorr of CH_4 was added into the major N_2 gas through a stainless steel capillary. Sample gas was ionized by a pulsed 2 keV electron beam. The ions produced were sampled through a slit made of razor blades. The width and the length of the slit were 10 μm and 1 mm, respectively. Since the width of the slit was smaller than the mean free path of a few torr sample gas, the ions were sampled through the slit by the molecular flow, i.e., the adiabatic cooling of the effusing gas during the ion sampling was negligible.

When the sample gas N_2 containing a small amount of CH_4 was ionized by a 2 keV electron beam, the $CH_3{}^+$ ion was formed by the charge-transfer reaction, $N_2{}^+ + CH_4 = CH_3{}^+ + H + N_2$. This reaction is exothermic by about 28 kcal/mol, and thus the nascent $CH_3{}^+$ ion may be internally excited to same extent. We think that the vibrationally hot primary product $CH_3{}^+$ may be quickly thermalized by the multiple collisions with buffer N_2 molecules. The methyl cation was found to be quickly converted to $H_3C^+(N_2)_1$ and no equilibrium between $CH_3{}^+$ and $H_3C^+(N_2)_1$ could be observed up to 550 K under the present experimental conditions. This is reasonable because the bond energy of $CH_3{}^+$–N_2 is reported to be more than 40 kcal/mol [4–6] and the measurement of the equilibrium for reaction (1) with $n = 1$ is beyond the capability of the present high-pressure mass spectrometer used. The measurements of the equilibrium constants for reaction (1) with $n \geq 2$ were made down to the temperature just above the condensation point of a few torr major gas N_2 (∼55 K). Thermochemical data (ΔG°, ΔH°, and ΔS°) were obtained by measuring the temperature dependence of the equilibrium constant K using the van't Hoff equation, $-\ln K = \Delta G^\circ/RT = \Delta H^\circ/RT - \Delta S^\circ/R$.

Cluster geometries of $H_3C^+(N_2)_n$ were determined with the B3LYP/6-311+G(d) method [10]. After full geometry optimizations, vibrational analyses were performed to check whether the geometries are correctly optimized for stable species and to obtain zero-point vibrational energies (ZPEs). Isomeric structures were carefully examined. Theoretical bond energies are composed of differences of B3LYP/6-311+G(d) electronic energies and ZPEs. For $n = 1$ and 2, G2(MP2) [11] energies were also calculated to assess the B3LYP/6-311+G(d) geometries and energies. All the calculations were carried out, using the GAUSSIAN 98 program [12] installed at the Compaq ES40 in the Information Processing Center (Nara University of Education).

3. Results and discussion

3.1. Experimental results

The results for the experimentally measured equilibrium constants for reaction (1) are displayed as the van't Hoff plots in Fig. 1. The enthalpy and entropy changes ($\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$) obtained from Fig. 1 are summarized in Table 1. The experimental errors for $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ in Table 1 were estimated by the method of least squares. Since this method did not take the systematic errors into account, the errors in $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ could be larger than those

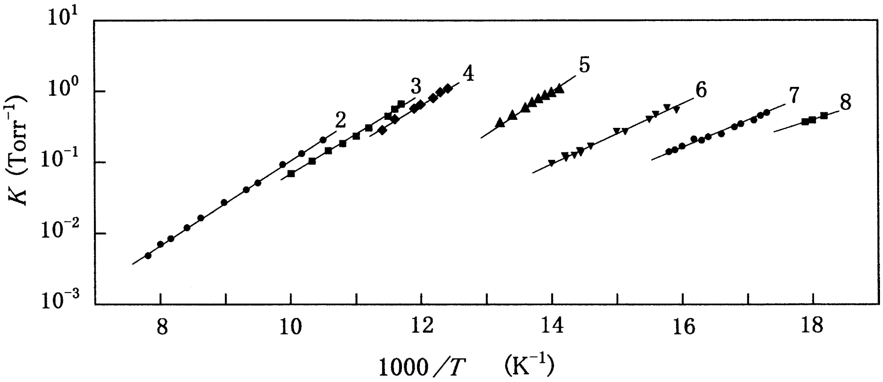


Fig. 1. Van't Hoff plots for the clustering reaction, $H_3C^+(N_2)_{n-1} + N_2 = H_3C^+(N_2)_n$.

Table 1
Experimental ($\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$) and calculated ($\Delta E_{n-1,n}$) thermochemical data for the gas-phase clustering reactions $H_3C^+(N_2)_{n-1} + N_2 = H_3C^+(N_2)_n$

n	$-\Delta H^\circ_{n-1,n}$	$-\Delta E_{n-1,n}$	$-\Delta S^\circ_{n-1,n}$
1	–	41.3 (42.6)	–
2	2.9 ± 0.3	2.5 (3.0)	20 ± 3
3	2.8 ± 0.2	2.3	20 ± 2
4	2.7 ± 0.3	2.3	21 ± 3
5	2.5 ± 0.2	2.0	22 ± 2
6	2.2 ± 0.2	1.5	23 ± 2
7	1.7 ± 0.2	1.5	18 ± 2
8	1.5 ± 0.4	1.3	16 ± 5

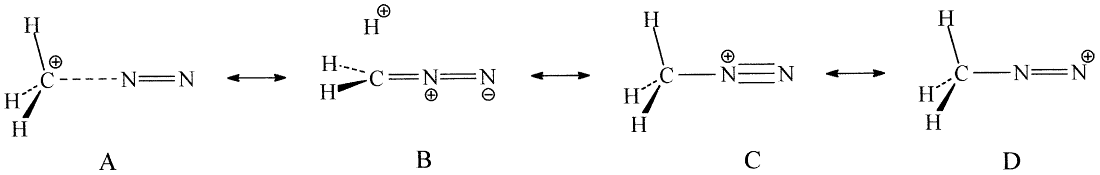
ΔH° and ΔE are in kcal/mol and ΔS° is in cal/mol K (standard state, 1 atm). $\Delta E_{n-1,n}$ values are theoretical energies calculated by B3LYP/6-311+G(d) electronic and zero-point vibrational ones. In parentheses, G2(MP2) enthalpy changes of $n = 1$ and 2 are also shown.

shown in Table 1. The plots with $n = 1$ could not be measured under the present experimental conditions due to the too large bond energy for H_3C^+–N_2. That is, a large gap in the van't Hoff plots exists between $n = 1$ and 2 in Fig. 1. In the figure, the plots with $n = 2$, 3, and 4 are very close to each other and there appears a gap between $n = 4$ and 5. This indicates that the cluster ion $H_3C^+(N_2)_n$ can be represented as the shell structure, $H_3C^+(N_2)_1(N_2)_3(N_2)_{n-4}$. It is worthwhile noting that the entropy changes show a steady increase up to $n = 6$ in Table 1 although the shell completion is likely with $n = 4$. That is, the $n = 5$ and 6, N_2 ligands have some more restricted freedom of motion than those with $n \leq 4$ in the cluster. This suggests that these two N_2 ligands may also be accommodated in the inner shell. This experimental finding is reasonably reproduced by the theoretical calculations as will be described in the following section.

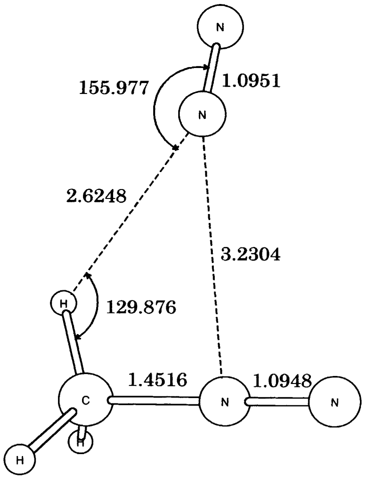
3.2. Computational results and discussion

Stabilities and structures of $H_3C^+(N_2)_n$ clusters are examined. When a nitrogen molecule is bound strongly to methyl cation, the cation character is delocalized as in Scheme 1. In fact, the $[H_3C–N_2]^+$ complex is isovalent with acetonitrile, $CH_3–C\equiv N$.

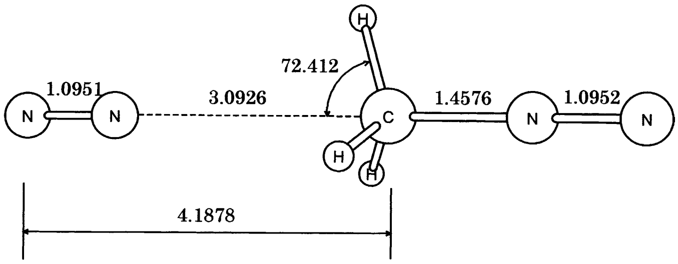
The large bond energy, $-\Delta E_{0,1}$(RB3LYP/6-311+G(d)) $= 41.3$ kcal/mol or $-\Delta E_{0,1}$(G2(MP2))



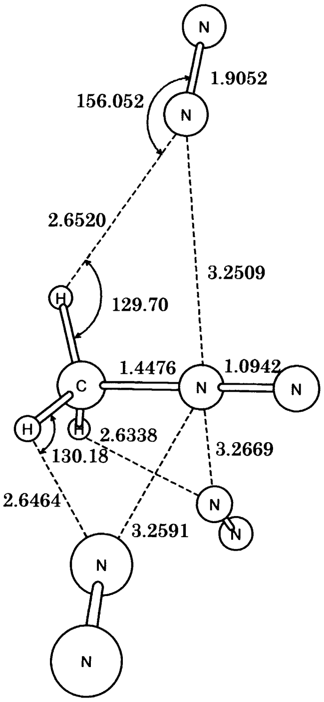
Scheme 1. Canonical resonance structures of $H_3C^+(N_2)_1$ for considering $H_3C^+(N_2)_n$ ($n \geq 2$) cluster geometries.

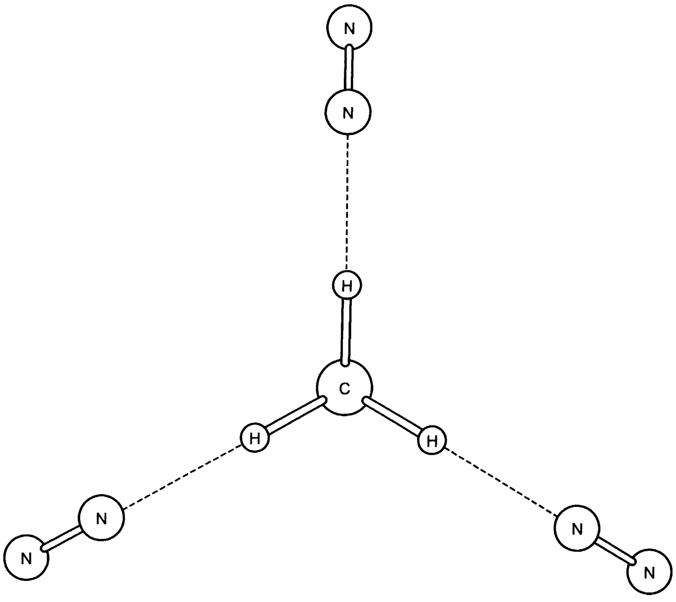


n=2a



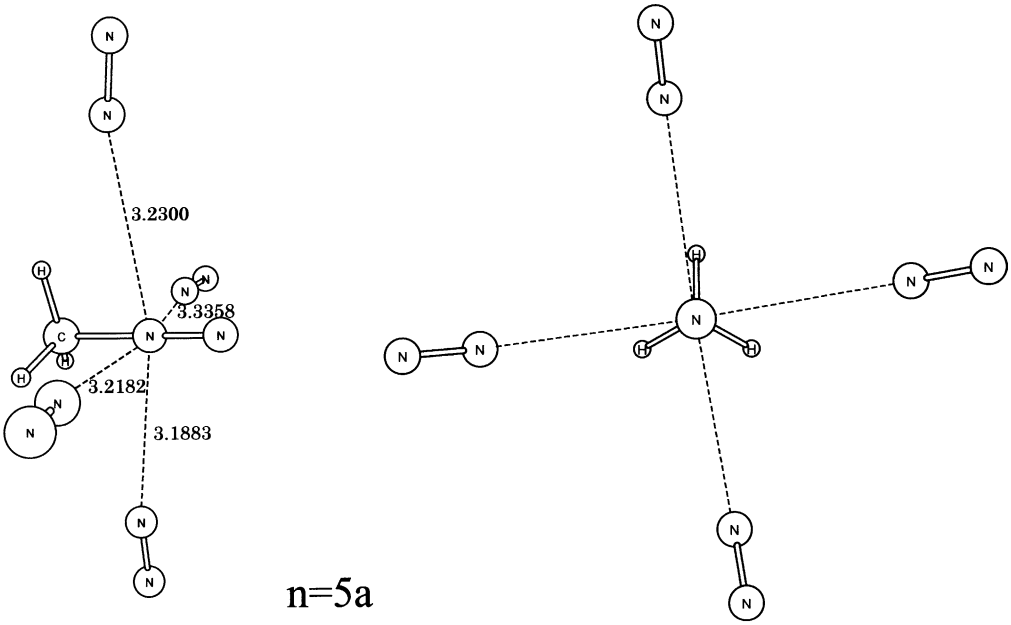
n=2b



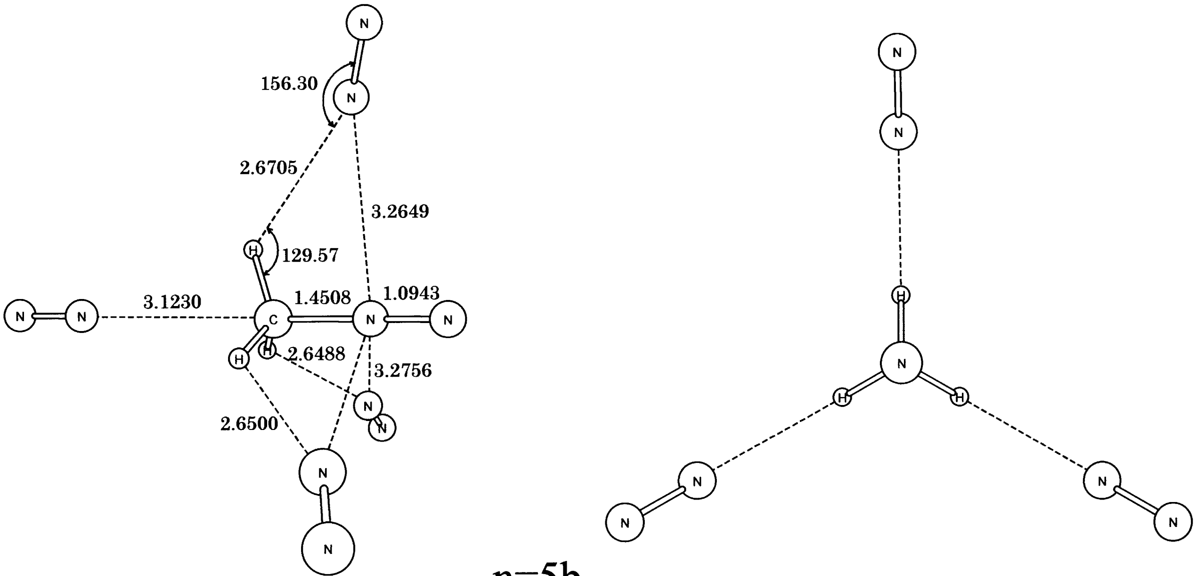


n=4a

Fig. 2. Geometries of $H_3C^+(N_2)_n$ optimized with RB3LYP/6-311+G(d). When geometric isomers are present (n = 2, 5, and 6), the stability order is $n_a > n_b > n_c$ (the isomer a is best). Geometries of n = 2a, 5c, and 6b are of C_s symmetry. Those of n = 2b, 4, 5b, and 8 are of C_{3v} one. Distances are in angstrom, and angles are in degree.



n=5a

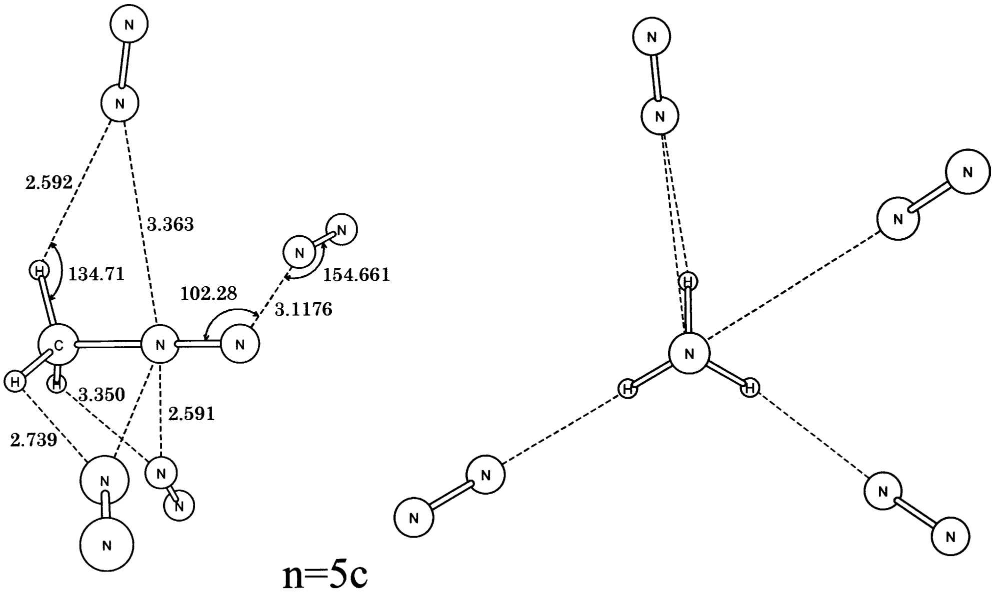


n=5b

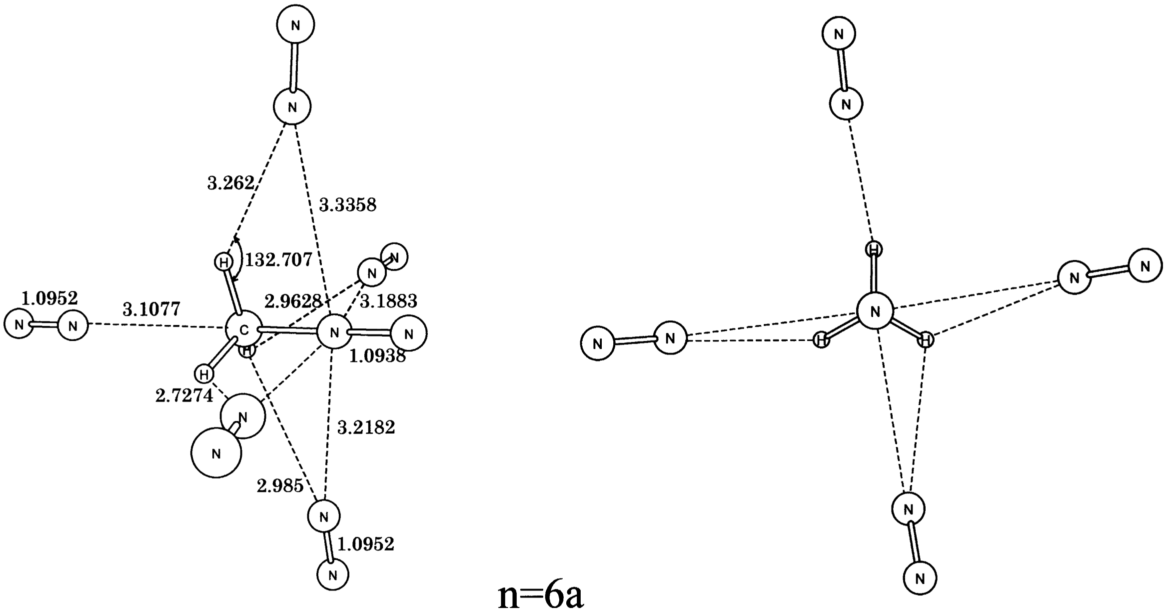
Fig. 2. (*Continued*).

= 42.6 kcal/mol, of $H_3C^+–N_2$ (Table 1) leads to the positive-charge delocalization. Fig. 2 shows representative (i.e., $n = 2$, 4, 5, 6, and 8) cluster geometries of $H_3C^+(N_2)_n$. For $n = 2$, there are two geometric isomers. The $n = 2a$ is more stable than the $n = 2b$ one. In the former geometries, the N_2 coordination is controlled by a coordination bond. In addition, the ligand N_2 molecule is polarized, which leads to the $N \cdots H$ hydrogen bond (Scheme 2).

Thus, the resonance structures B and C in Scheme 1 determine the $n = 2a$ geometry. The first shell is completed by the three-fold coordination in



n=5c

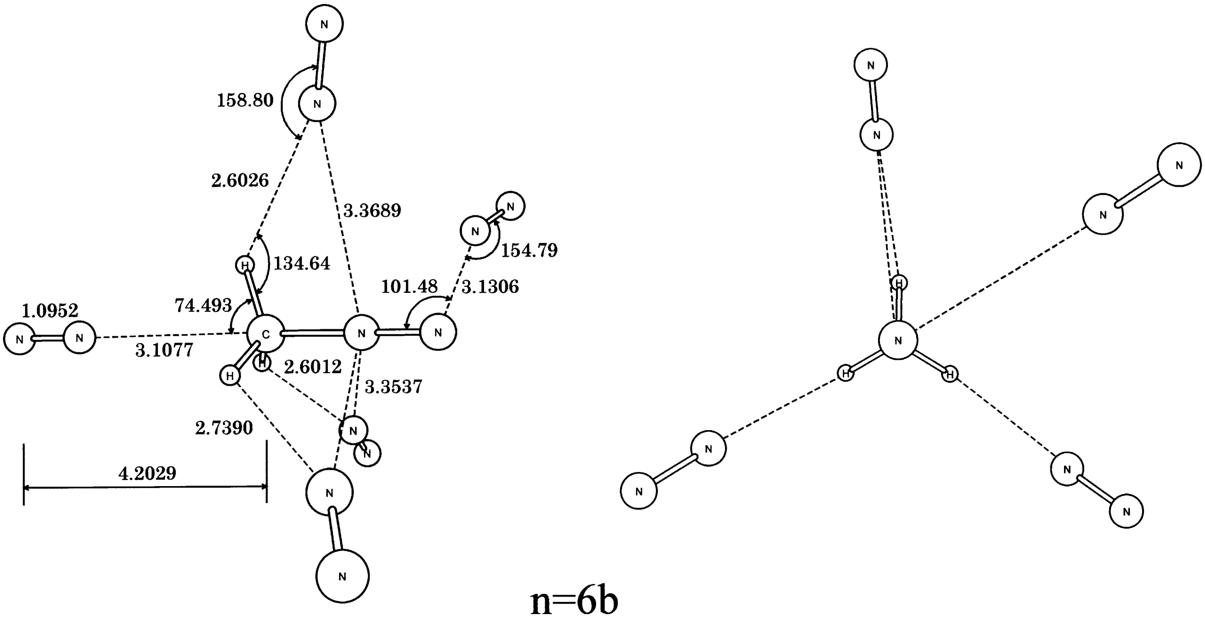


n=6a

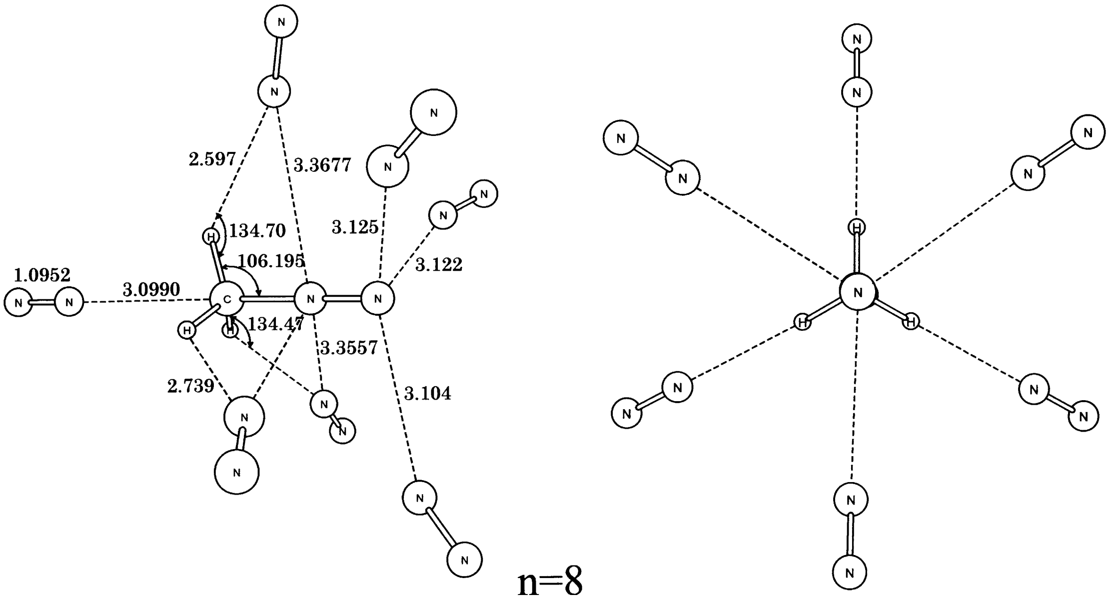
Fig. 2. (*Continued*).

$H_3C^+(N_2)_1(N_2)_3$, i.e., $n = 4$ (Fig. 2a). The $n = 4$ geometry is of C_{3v} symmetry. The shell formation of $n = 4$ is consistent with the similar $\Delta H^\circ_{n-1,n}$ values for $n = 2$, 3, and 4 (Table 1).

For $n = 5$, three isomers were obtained (Fig. 2b). The $n = 5$a geometry is composed of orthogonal coordinations of four N_2 molecules. Two orthogonal $2p_\pi$ vacant orbitals are linked with lone-pair orbitals of



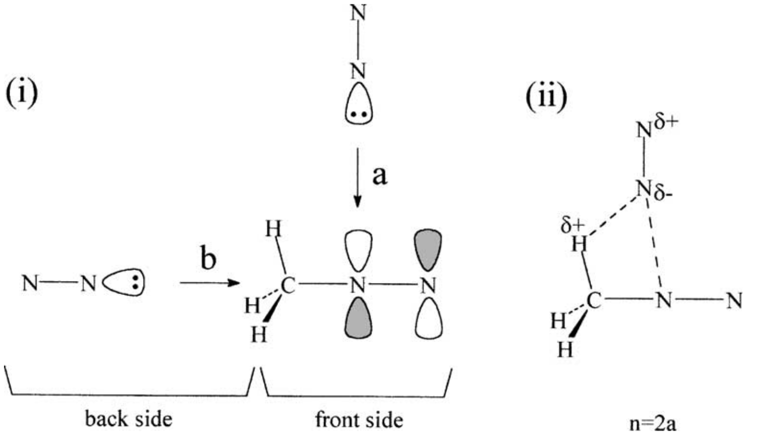
n=6b



n=8

Fig. 2. (*Continued*).

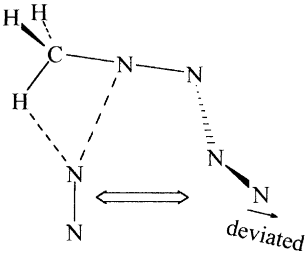
ligand molecules. The coordination sacrifices slightly the three-fold orientation of three methyl C–H bonds. In $n = 5b$, the fifth N_2 is linked with the carbon atom at the back side (C_{3v} symmetry conserved). In $n = 5c$, the fifth one is bound to the right-terminal nitrogen atom of $H_3C^+(N_2)_1$ according to the resonance structure D in Scheme 1. The fifth N_2 undergoes the ligand–ligand exchange repulsion and the coordination



Scheme 2. The $n = 2$ N_2 orientation toward $CH_3^+(N_2)_1$. (i) Two possible coordinations, a and b. (ii) The $CH_3^+(N_2)_2$ geometry made from the orientation a assisted by the H···N hydrogen bond.

is deviated from the charge-transfer controlled line (Scheme 3).

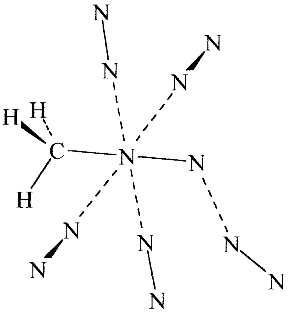
Although the stability order of $n = 5a > 5b > 5c$ is predicted, the energy differences are small (0.2 kcal/mol for $n = $ 5a–5b and 0.6 kcal/mol for $n = $ 5a–5c). Three isomers of $n = 5$ are less favorable than $n = 4$ with good three-fold orientation. Fig. 2c shows geometries of $n = 6$ and 8. Since the orthogonal coordinations of four N_2 molecules make the front side crowded, the sixth N_2 is situated at the back side of the methyl group ($n = $ 6a). It is noteworthy that the "$n = $ 6c" geometry could not be obtained, because of the steric repulsion between the four-fold coordinated N_2 molecules and the sixth one which is bonded to the right-side terminal N atom (Scheme 4).



Scheme 3. The ligand–ligand exchange repulsion to distort the standard linear coordination.

For $n \geq 7$, only the coordination to the terminal N atom is possible. Therefore, the four-fold coordination at the central N atom of $H_3C^+(N_2)_1$ must be relaxed to the three-fold one to reduce the steric congestion at the front side. Thus, the double three-fold coordinations give rise to the second saturation shell. The C_{3v} symmetry is recovered. In view of the clustering process, resonance structures C and B contribute dominantly to the N_2 ($n \geq 2$) coordination. Methyl C–H bonds regulate the three-fold coordinations.

In Table 1, the computed bonding energies, $\Delta E_{n-1,n}$ are in excellent agreement with present experimental ones, $\Delta H^\circ_{n-1,n}$.



n=6c, absent

Scheme 4. The $n = $ 6c model composed of the four-fold coordination to the central nitrogen atom and a terminal one. The model could not be obtained due to the steric congestion at the front side.

4. Concluding remarks

This work has dealt experimentally and theoretically with the gas-phase clustering reaction (1). The G2(MP2) calculation shows that the $H_3C^+\cdots N_2$ bond energy is 42.6 kcal/mol. Owing to the large energy, the resultant $n = 1$ cluster has a delocalized charge distribution and may be regarded as an acetonitrile molecule, $H_3C{-}C{\equiv}N$. Therefore, bonding energies of $n \geq 2$ are only in a few kcal/mol. In spite of those small energies, the pattern of the fall-off of bonding energies with n indicates that the $H_3C^+(N_2)_4$ species is a shell. The shell conforms to the $H_3C^+(N_2)_1(N_2)_3$ structure, which consists of the three-fold coordination of $n = 2$, 3, and 4 ligands according to hydrogen bonds with three methyl-group hydrogens. B3LYP/6-311+G(d) calculations made good performance to reproduce the small bonding energies. “A few kcal/mol energy” should have more precision than before by experimental–theory combination studies.

References

[1] K. Hiraoka, J. Katsuragawa, T. Sugiyama, A. Minamitsu, S. Yamabe, H. Kouno, Chem. Phys. Lett. 271 (1997) 302.
[2] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (Suppl. 1) (1988).
[3] K. Hiraoka, I. Kudaka, S. Yamabe, Chem. Phys. Lett. 178 (1991) 103.
[4] M.S. Foster, A.D. Williamson, J.L. Beauchamp, Int. J. Mass Spectrom. Ion Phys. 15 (1974) 429.
[5] J.K. Hovey, T.B. McMahon, J. Phys. Chem. 91 (1987) 4560.
[6] T.B. McMahon, T. Heinis, G. Nicol, J.K. Hovey, P. Kebarle, J. Am. Chem. Soc. 110 (1988) 7591.
[7] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.
[8] P. Kebarle, in: J.M. Farrar, W.H. Saunders (Eds.), Techniques for the Study of Ion–Molecule Reactions, Wiley, New York, 1988.
[9] K. Hiraoka, J. Chem. Phys. 87 (1987) 4048.
[10] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[11] L.A. Curtiss, K. Raghavachari, J.A. Pople, J. Chem. Phys. 98 (1993) 1293.
[12] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.