

## Pulsed laser photolysis of cyanuric triazide

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We have identified all-nitrogen cations by MS/MS spectrometry from pulsed laser irradiation of cyanuric triazide. There were the fragment peaks which may be composed only of nitrogen atoms (atomic mass is 14) in the first MS (MS1). Especially, the peak at mass 70 was strong. Successively, the second MS (MS2) showed that the fragment of mass 70 is composed of the ingredient of mass 14. Similar results were also obtained from the experiment with the cyanuric triazide labeled with  $^{13}\text{C}$ . Accordingly, the fragment of mass 70 ( $14 \times 5$ ) is identified to  $\text{N}_5^+$  which is considered to have covalent bonds.

## 1. Introduction

The recent discovery of new allotropic forms of carbon has also stimulated a renewed search for new allotropic forms of nitrogen<sup>1~9)</sup>. However, polynitrogen compounds,  $\text{N}_n$ , where  $n$  exceeds 3, have so far not been prepared. An important motivation for the research is the possibility that such nitrogen allotropes can be used to store energy. The dissociation energy of  $\text{N}_2$  ( $\text{N} \equiv \text{N}$  triple-bond energy) is 225 kcal/mol, while the standard  $\text{N}=\text{N}$  double-bond energy is 100 kcal/mol and that of the  $\text{N}-\text{N}$  single bond is about 40 kcal/mol. Since the  $\text{N} \equiv \text{N}$  triple-bond energy is much more than three times the single-bond energy, this argument suggests that the  $\text{N}_n$  clusters with all  $\text{N}-\text{N}$  single-bonds may release significant amounts of energy when they dissociate into  $\text{N}_2$  molecules. From the preliminary investigation<sup>10)</sup> by using semi-empirical molecular orbital calculations such as AM1 and PM3 methods, it is shown that the explosion energy

of the  $\text{N}_n$  clusters is much more than that of TNT (trinitrotoluene). Furthermore, the  $\text{N}_n$  clusters would be particularly a good rocket propellant composition, because they generate a large amount of clean nitrogen gas without oxygen. The  $\text{N}_n$  clusters with  $\text{N}=\text{N}$  double-bonds may also release much amount of energy. Thus, the allotropes except 'normal' dinitrogen should be one of ideal explosives.

Many polynitrogen and nitrogen-rich systems have been investigated extensively at various levels of theory<sup>1~9)</sup>. Previously calculated but presently still unknown polynitrogen ( $n > 3$ ) compounds include  $\text{N}_4$ ,  $\text{N}_5$ ,  $\text{N}_6$ ,  $\text{N}_8$ ,  $\text{N}_{12}$ ,  $\text{N}_{20}$  and so on. Especially, much of the published work is concentrated on  $\text{N}_4$  and  $\text{N}_6$ <sup>5~9)</sup>. At high theoretical levels, an open chain structure of  $\text{N}_4$  is the lowest energy isomer. The lowest energy cyclic  $\text{N}_6$  minimum is not the benzene-like  $D_{6h}$  but the  $D_2$  twist-boat form. Furthermore, the most stable isomer of  $\text{N}_6$  has an open-chain structure. However, polynitrogen compounds,  $\text{N}_n$ , where  $n$  exceeds 3, have so far not been prepared. In 1980, Vogler et al. suggested the formation of hexaazabenzene in the photochemical reductive elimination of *cis*- $[\text{Pt}(\text{N}_3)_2(\text{PPh}_3)_2]$ <sup>11)</sup>. However, there has

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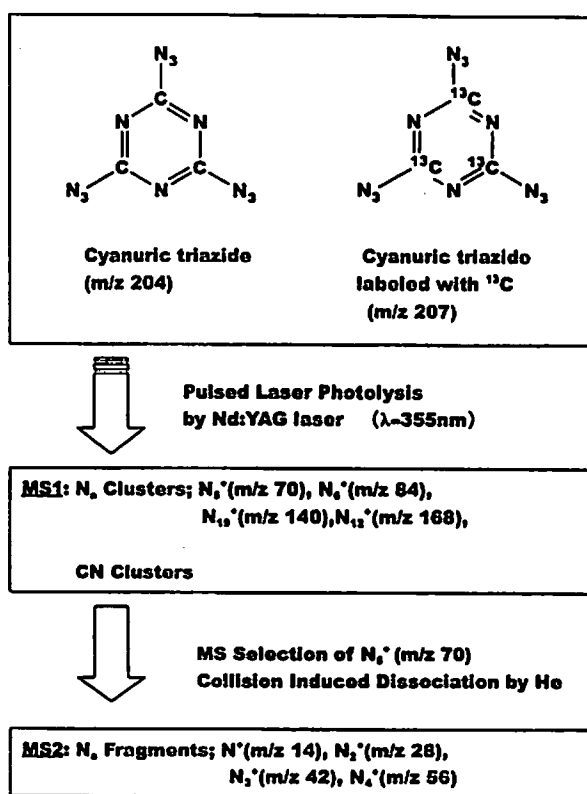
never been the evidence that the species are composed only of nitrogen atoms and have covalent bonds. On the other hand, van der Waals clusters of nitrogen, such as  $(N_2)_n^+$  and  $N(N_2)_n^+$ , have been widely studied by secondary ion mass spectrometry (SIMS)<sup>13-15</sup>. The clusters are formed in a supersonic nozzle expansion of nitrogen ( $N_2$ ) and connected together by weak van der Waals forces. Therefore, van der Waals clusters of nitrogen are not of interest as energetic materials.

We investigated pulsed laser photolysis of cyanuric acid by MS/MS spectroscopy, in order to find the possibility of generation of polynitrogen.

## 2. Experimental

We have identified polynitrogen cations by MS/MS spectrometry<sup>12</sup> from pulsed laser photolysis of cyanuric triazide ( $C_3N_3$ )<sup>16</sup>. We selected cyanuric triazide as a starting reactant of polynitrogen compounds, because we needed the condition where reactive nitrogen species, instead of stable  $N_2$  and  $N_3^-$ , can be generated. Inorganic azides, such as sodium azide ( $NaN_3$ ), may not be adequate. Cyanuric triazide should be a good candidate, because cyanuric triazide is highly reactive and the cyano group is highly electron-withdrawing, so we predicted that the compound decomposed into reactive nitrogen species rather than  $N_2$  or  $N_3^-$ . Moreover, polynitrogen compounds should be easily identified, because cyanuric triazide is composed of two elements, that is, nitrogen and carbon. Cyanogen azide,  $NC-N_3$ , is also one of candidates, but this gaseous compound is less stable than cyanuric triazide.

Cyanuric triazide<sup>17</sup> was purified and solved in acetone. The solution was applied to a high-purity metal plate and dried out. Silicon, silver, and stainless plates were used. Then, the plate with the laminar cyanuric triazide was put into a vacuum chamber. The cyanuric triazide was photolyzed and ionized by a Nd:YAG pulsed laser (third harmonic generation;  $\lambda=355$  nm, full width at half-maximum; 10 ns, 30 Hz, 400  $\mu$ J/pulse) at room temperature. The ionized fragments were investigated by MS/MS. All measurements were carried out in the positive ion



Scheme 1 Outline of the identification of nitrogen clusters

mode using a JEOL (Tokyo, Japan) HX/HX110A four-sector tandem mass spectrometer of EB/EB configuration. The resolution of both mass spectrometers was approximately 1000. In second MS (MS2) experiments, helium gas was introduced into a collision chamber biased at 7 kV to the pressure leading to a 50% attenuation of precursor ions (*He* collision-induced dissociation (CID)). The spectra were recorded by a JEOL DA7000 data system.

## 3. Results and discussion

Scheme 1 is an outline of the identification of nitrogen cluster. As shown in Fig. 1, there are the fragment peaks which may be composed only of nitrogen atoms (atomic mass is 14) in the first MS (MS1). Of all the peaks at mass  $14 \times n$  ( $n > 3$ ), the peaks at mass  $14 \times 4$  (m/z 56) and  $14 \times 5$  (m/z 70) are strong. The peaks at mass  $14 \times 6$  (m/z 84),  $14 \times 10$  (m/z 140),  $14 \times 12$  (m/z 168) are medium and the peaks at mass  $14 \times 9$  (m/z 126),  $14 \times 14$  (m/z 196) are weak. Caution should be exercised that methylene  $CH_2$  is also atomic mass 14 and silicon is atomic mass 28. Successively, the daughter fragments of the par-

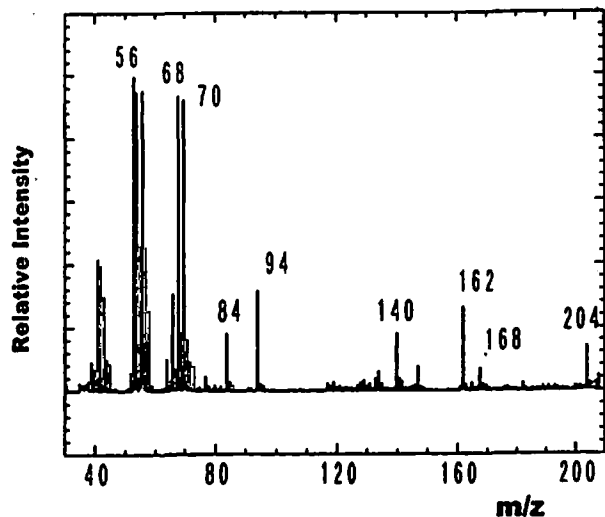


Fig. 1 The first mass spectrometry of cyanuric triazide photolyzed by pulsed Nd:YAG laser. Peaks at mass  $14 \times n$  are found. The peak at mass 204 is  $M^+$ .

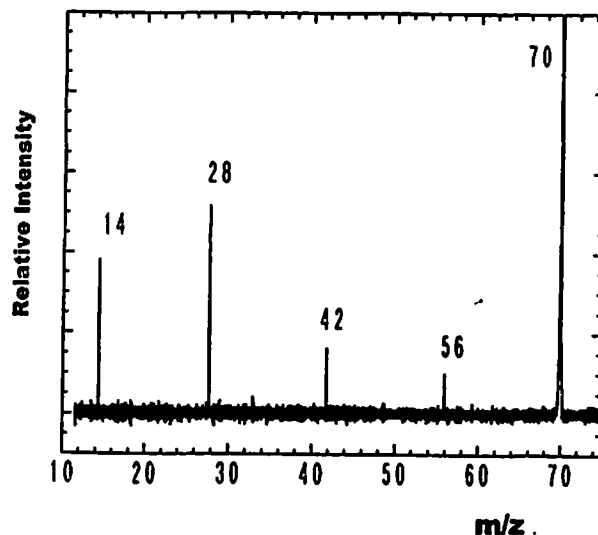


Fig. 2 Collision induced dissociation mass spectrometry (MS2) of the parent fragment at mass 70. Obviously, the fragment of mass 70 is composed of nitrogen.

ent fragment at mass  $14 \times 5$  were measured by the second MS (MS2). The MS2 spectrum is shown in Fig. 2. Obviously, the fragment of mass  $14 \times 5$  is composed of the ingredient of mass 14. Furthermore, cyanuric triazide labeled with  $^{13}\text{C}$  was also measured by the same procedure. As

a result, the peak at  $14 \times 5$  was also shown in the first MS spectrum and the second MS spectrum was similar to Fig. 2. Accordingly, the fragment of mass  $14 \times 5$  is  $\text{N}_5^+$ . The pulsed laser desorption is effective and indispensable, because any nitrogen clusters have neither been found by

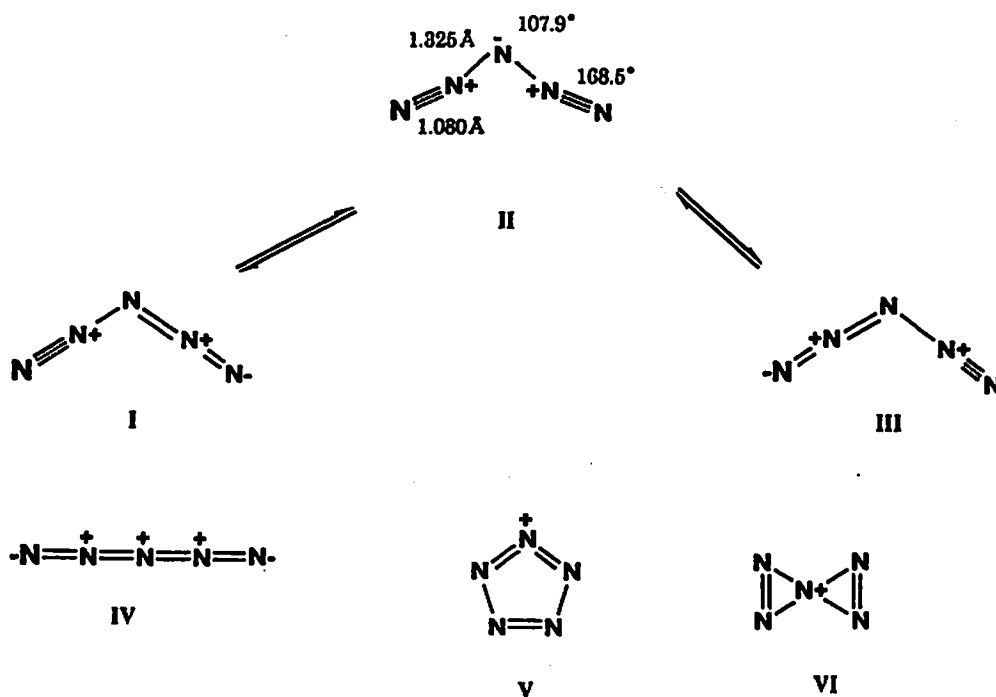


Fig. 3 Possible molecular structures of  $\text{N}_5^+$ . I, II, III are chain-forms. IV is a linear-form. V is a 5-member-ring. VI is a spiro-form. The bond length and the bond angle of II were calculated by the *ab initio* MO calculation at HF/6-31G\*.

MS/MS from the collision induced dissociation with helium nor by MS from electron impact ionization. The silicon plate used gave good results where strong peaks at  $14 \times n$  were shown. However, it is ambiguous that clusters of nitrogen and silicon,  $\text{Si}_m\text{N}_n$  have peaks at mass  $28m+14n$ . In order to avoid the confusion, we used the silver and stainless plate and we confirmed that there was the peak at 70, although the height of the peak was lower than that with silicon plate. About other fragments, such as  $\text{N}_4$ ,  $\text{N}_6$ ,  $\text{N}_8$ ,  $\text{N}_{10}$ ,  $\text{N}_{12}$ , and  $\text{N}_{14}$ , their MS2 spectrum are not measured, because their intensities of MS1 are too low.

The structure and electronic state of  $\text{N}_5^+$  are unknown at present. However, generally, weakly connected van der Waals clusters should be broken by the *He* CID. Moreover, as  $\text{N}_n^+$  ( $n=1-5$ ) were detected equivalently as shown in Fig. 2, the  $\text{N}_5^+$  is considered to be not a Van der Waals cluster such as  $(\text{N}_2)(\text{N}_3^+)$  or  $(\text{N}_2)_2(\text{N}^+)$ , but a molecular ion which has covalent bonds. Possible covalent-bonded molecular structures are shown in Fig. 3. From our ab initio MO calculations, the stationary points of a five-member ring molecule (V) and that of a spiro molecule (VI) have not been found. A linear molecule (IV) has been stable energetically, but has two imaginary frequencies. Thus, a linear molecule would be unstable. From the result at HF/6-31G\* level, a chain molecule has been stable energetically and vibrationally. The bond lengths and bond angles at HF/6-31G\* level are also described in Fig. 3 (II). However, at MP2/6-31G\* level, the stationary point of the chain structure has not been found. The molecular structure of  $\text{N}_5^+$  will be determined experimentally in the future.

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- 17) *Warning! Cyanuric triazide is very sensitive to heat, impact and friction and easily explode. The compound should never be prepared or handled by anyone untrained in proper safety precautions. All work in connection with the compound should be done only by experienced personnel and only with appropriate environmental safeguards.*



## シアヌール酸トリアジドのパルスレーザー光分解

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新しいポリ窒素化合物を探索するために、シアヌール酸トリアジドをパルスレーザー光分解させて生成物をMS/MSにより確認した。まず、基板上に塗布したシアヌール酸トリアジドにNd:YAGレーザーを照射し、発生したイオンを1次MSにより検出すると窒素だけからなると思われるフラグメントがいくつか見られた。その中で特に強いピークである $m/z$  70のフラグメントを再度、ヘリウムの高速衝突により分解させ、質量分析(2次MS)したところ、それは質量数14からなることがわかった。炭素同位体 $^{13}\text{C}$ を用いた実験および基板の材質を変えた実験でも、同様の結果が得られた。したがって、 $m/z$  70に相当するフラグメント $\text{N}_5^+$ であることが示された。このフラグメントのMS2スペクトルは14毎に等価に解離しているため、Van der Waalsクラスターではなく、共有結合を持つクラスターである可能性が高い。

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