

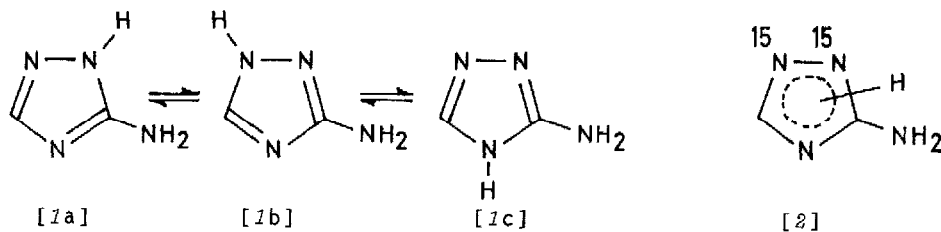
CID EXPERIMENTS ON *C*-AMINOTRIAZOLE^{*}.

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We have previously described¹ the mass spectra of isomeric ethylamino-triazoles in order to define the structure of *C*-aminotriazole 1 in the gas phase. Kinetic energy releases associated with ethylene losses, thermochemical and kinetic isotope effects measurements showed the formation of isomeric aminotriazoles ions which isomerized into an unknown common structure (identical to the molecular ion of aminotriazole 1) before fragmentation. This paper presents some new results on this subject using nitrogen 15 labeling and also high kinetic energy ion - molecule reactions (CID spectra)².



C-aminotriazole-1,2-¹⁵N 2 is synthesized by reaction of hydrazine-¹⁵N₂ sulfate on *S*-methylisothiurea sulfate followed by cyclisation with formic acid³. In order to obtain workable quantities of the product, labeled hydrazine is diluted in 90 % unlabeled hydrazine. This procedure does not prevent accurate analysis of the mass spectrum of the labeled material because, with a reversed geometry mass spectrometer, it is possible to select the molecular ion of 2 and then to study the uni- or bimolecular fragmentations in the second field free region. In some favourable cases, carbon 13 natural abundance has been used to derive ion structures⁴.

The MIKE spectrum (VARIAN MAT 311 A : 70 eV, 3 KV) of the molecular ion of **2** shows only one fragmentation : the loss of unlabeled hydrogen cyanide. As earlier deuteration experiments showed that the exocyclic amino function is excluded from this reaction, this result suggests that the 2-amino-1,3,4-triazole **1b** tautomer does not represent the reactive structure of **1**.

The CID spectra of the molecular ions of **1** and **2** are given in figure 1.

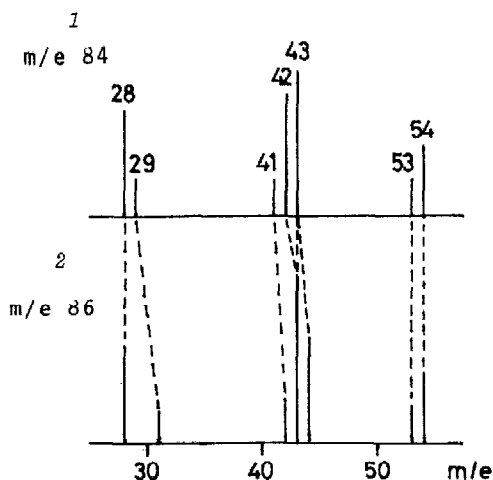


Figure 1 : Collision induced dissociations for the molecular ions **1** and **2**.

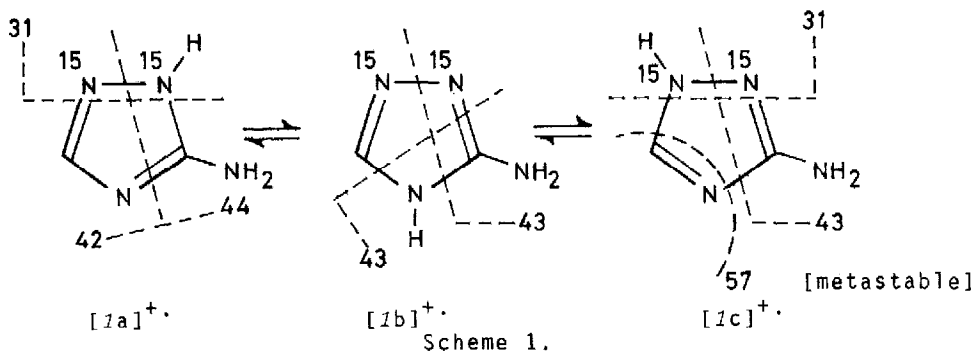
The gas (air) pressure in a small collision chamber located at the focal point of the second field free region⁵ is increased to about 10^{-4} Torr corresponding to an attenuation of the main beam of 20-30 %.

In addition to the intense unimolecular loss of HCN, seven new fragment ions are observed. The shift of the peaks from **1** to **2** determines the compositions of these fragment ions (Fig. 1).

It has been stated⁶ that i) the CID method gives results which do not depend on the initial excitation of the ion and

ii) rearrangement reactions are minimized in such a way that these bimolecular processes are quite characteristic of the stable ions sampled.

On the basis of this second statement, we may try now to relate the CID fragment ions of **2** with the structure of the precursor(s). (scheme 1).



The fragment ion m/e 44 comes from tautomer 1a ; m/e 43 ($\text{CH}_3\text{N}_2 + \text{CH}_2\text{N}^{15}\text{N}$) from 1b or 1b and 1c ; m/e 42 from 1a ; m/e 31 from 1a or 1c.

The formation of m/e 28 fragment ion involves probably the exocyclic amino group and this fragmentation is equally probable for the three tautomers. The two last fragments (m/e 54 and 53) are more difficult to interpret, the labeled nitrogens being lost with 2 or 3 hydrogens.

Note also that tautomers 1a or 1c may be responsible for the unimolecular loss of HCN, but, in agreement with earlier work on triazoles^{7,8}, the fragmentation shown in scheme 1 for 1c seems more likely. All these CID results suggest that the fragments m/e 43 and m/e 42 have a protonated cyanamide and cyanamide structure respectively.

In fact these two ions are observed in the mass spectrum of 1. If the position of the hydrogens are not taken into account, two different skeletons are possible : the first one showing a C-N-N (I) sequence in which the two nitrogens are bonded and a second N-C-N (II) sequence where they are separated by a carbon atom (a cyclic species being considered just like the C-N-N sequence).

The MIKE spectrum of the $[\text{M}-\text{HCN}]^+$ ions (m/e 42 ; C-N-N sequence) of 1,2,4-triazole⁹ shows a dish-topped metastable peak corresponding to the loss of N'. Moreover, the CID spectra of this ion and the corresponding ion of aminotriazole are totally different suggesting the occurrence of a cyanamide structure in the last case.

The m/e 43 ion from 1 has also been compared with a methyl diazonium cation derived from 1,2-dimethyl-3,6-diphenyldihydro-tetrazine¹⁰ : the different CID spectra obtained are in agreement with a N-C-N sequence (protonated cyanamide structure) in the case of 1.

These observations are thus compatible with proposed CID fragmentations shown in scheme 1.

In conclusion, the molecular ion of *C*-aminotriazole consists of an equilibrated mixture of tautomeric ions as shown by high kinetic energy ion-molecule reactions. The metastable molecular ions could have the structure 1a, but structure 1c seems more likely.

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