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Mendeleev Commun., 2018, **28**, 470–471

Mendeleev Communications

Electron impact generation of tetraazidocyclobutadiene radical cation from tetraazidopyridine-2-carbonitrile

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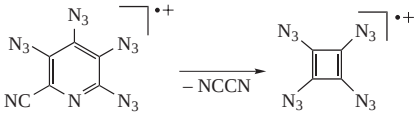
DOI: 10.1016/j.mencom.2018.09.005

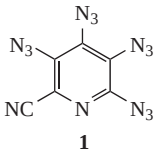
Upon electron impact, tetraazidopyridine-2-carbonitrile releases cyanogen to form tetraazidocyclobutadiene radical cation as the first representative of azido-substituted cyclobutadiene derivatives.



Upon electron impact (EI), many pyridines lose hydrogen cyanide to form cyclobutadiene radical cations as the primary fragmentation products.[1] The elimination of HCN takes place even from 2-cyanopyridine ion that may theoretically also release neutral cyanogen (NCCN).[2] At the same time, all known to date ionized azidopyridines never release HCN or NCCN at the initial stage of fragmentation due to much more facile decomposition of the azido groups. For instance, the molecular ions of 3,4,5-triazidopyridine-2,6-dicarbonitrile[3] and 2,3,5,6-tetraazidopyridine-4-carbonitrile[4] eliminate N_2 to form the corresponding $[M-N_2]^{\bullet+}$ ions. Therefore, azido-substituted cyclobutadiene radical cations remain so far unknown.

Recently, we have reported on the synthesis,[5] thermolysis,[6] and ^{13}C and ^{15}N NMR spectra[7] of tetraazidopyridine-2-carbonitrile **1** possessing extremely high sensitivity toward heat and mechanical stimuli. The rate of its thermal decomposition is 1000 times higher than that of many other azidopyridines.[6,8] These data indicated another mechanism of the thermal decomposition of tetraazide **1**, in which dissociation of the $N–N_2$ bonds in the azido groups is not anymore the rate-determining stage. According to published data,[9] important information about the thermal decomposition of aryl azides can be obtained from the mass spectra of these compounds. Therefore, we have studied herein the fragmentation of compound **1** upon EI.

The EI mass spectrum† of tetraazide **1** differs drastically from those of all known aromatic azidopyridines (Figure 1). First of all, this spectrum displays an extraordinarily weak peak of molecular ion at *m*/*z* 268, indicating a very low stability of $[\mathbf{1}]^{\bullet+}$. Secondly, the base peak in the spectrum corresponds to cyanogen ion, *i.e.* $NCCN^{\bullet+}$, that should be the major product of decomposition of $[\mathbf{1}]^{\bullet+}$. Thirdly, the presence of the high-molecular-weight ion with *m*/*z* 216 demonstrates that the first step of fragmentation of $[\mathbf{1}]^{\bullet+}$ involves unprecedented elimination of NCCN. Finally, the peaks at *m*/*z* 104, 78, 64, 42 and 38 suggest that there are several parallel pathways of fragmentation of $[\mathbf{1}]^{\bullet+}$.



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Density functional theory (DFT) calculations‡ revealed that the molecular ion $[\mathbf{1}]^{\bullet+}$ has a pronounced quinonoid structure $[\mathbf{1\text{-}Q}]^{\bullet+}$ (Scheme 1). Therefore, the fragmentation of $[\mathbf{1\text{-}Q}]^{\bullet+}$ is very similar to that of substituted 1,4-benzoquinone ions.[10] Thus, the decomposition of the azido groups and fragmentation of the ring (pathway *a*) in $[\mathbf{1\text{-}Q}]^{\bullet+}$ to form the $[C_3N_3]^+$ ion are absolutely identical to the processes observed in the mass spectrum of 2,6-diazido-3,5-dicyano-1,4-benzoquinone.[11] DFT and high-level CCSD(T) calculations‡ showed that the most stable structure of $[C_3N_3]^+$ corresponds to the NC–N=C$^+$–CN ion resulting from the barrierless rearrangement of $(NC)_2C{=}N^+$. Another way of fragmentation of $[\mathbf{1\text{-}Q}]^{\bullet+}$ involves the decomposition of the azido groups and the elimination of NCCN (pathway *b*) to form $[C_4N_4]^{\bullet+}$ ion. This fragmentation mode is also typical of many substituted 1,4-benzoquinone ions.[10] The most probable structure

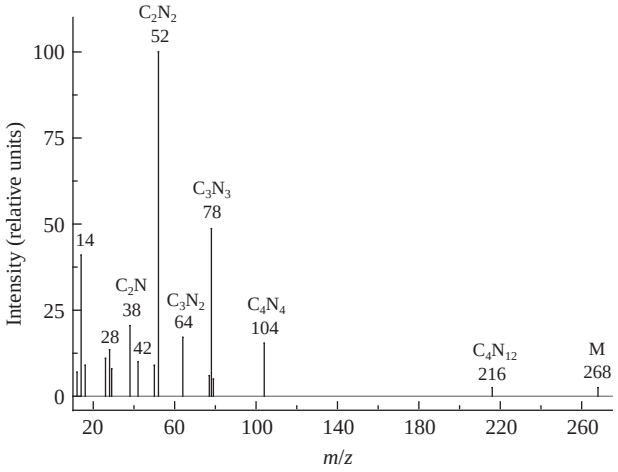
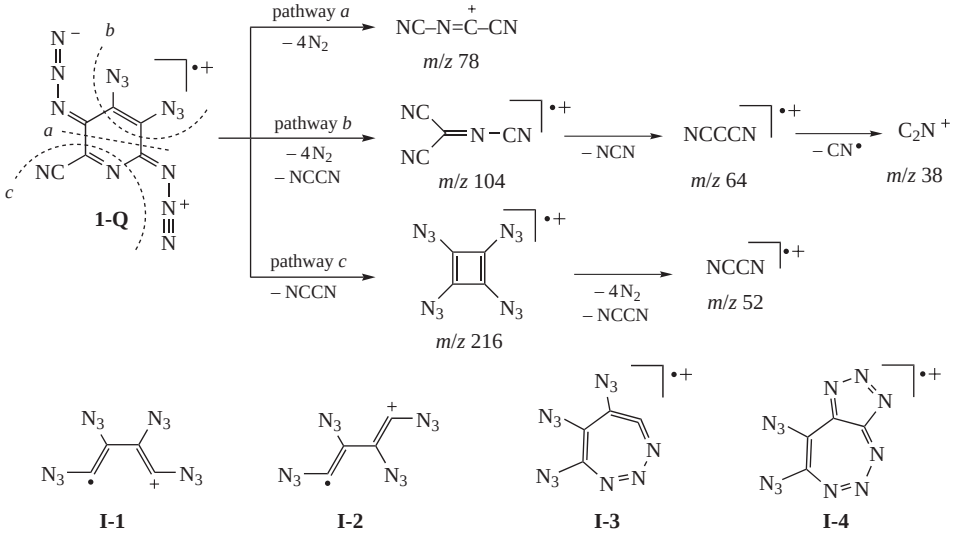


Figure 1 Electron impact mass spectrum of tetraazidopyridine-2-carbonitrile **1**.

† Compound **1** was synthesized according to the reported procedure.[5] Electron impact mass spectrum (70 eV, direct insertion, vacuum 10^{-4} Torr, source temperature 150 °C, sample temperature 100 °C) was recorded on a Finnigan MAT Incos 50 mass-spectrometer. MS (EI, 70 eV) *m*/*z* (%): 268 (2.5) $[M]^+$, 216 (2.5), 104 (15), 79 (4), 78 (49), 76 (5), 64 (17), 52 (100), 50 (6), 42 (7), 38 (21), 29 (6), 28 (14), 26 (10), 16 (10), 14 (41), 12 (9). Since the starting tetraazide **1** consists only of C and N atoms, the nominal mass of each ion in the low resolution mass spectrum of compound **1** corresponds to a single combination of C and N atoms, thus allowing one to determine as well the exact molecular formulas of these ions without the use of the high resolution mass spectrometry technique.



Scheme 1

of $[C_4N_4]^{\bullet+}$ corresponds to the $(NC)_2C{=}N{-}CN^{\bullet+}$ ion [its geometry and vibrational frequencies were calculated by DFT and CCSD(T) methods‡]. This ion eliminates NCN to form the $NCCCN^{\bullet+}$ ion. Previously, elimination of NCN from $(NC)_2C{=}N{-}CN^{\bullet+}$ to afford $NCCCN^{\bullet+}$ was observed in the mass spectrum of 2,3,5,6-tetraazidopyridine-4-carbonitrile.[4] Finally, the elimination of NCCN (pathway *c*) from $[\mathbf{1\text{-}Q}]^{\bullet+}$ prior to the decomposition of the azido groups may be considered just as an alternative to pathway *b*. This reaction has no analogies in the literature. First of all, it demonstrates that elimination of N_2 from molecular ions of aromatic azides does not always precede the fragmentation of the aromatic ring. Secondly, it shows that the fragmentation of some pyridine ions may start with the elimination of NCCN. According to DFT calculations,‡ the *cis*-butadiene radical cation **I-1** (see Scheme 1), expected after the elimination of NCCN from $[\mathbf{1}]^{\bullet+}$, is unstable and undergoes cyclization to form tetraazidocyclobutadiene radical cation (see Figure S3, Online Supplementary Materials). The *trans*-butadiene radical cation **I-2** is also unstable; it releases N_2 without a barrier. We studied theoretically a number of cyclic isomers of the $[C_4N_{12}]^{\bullet+}$ ion, other than tetraazidocyclobutadiene, including isomers **I-3** and **I-4**. It was found that alternative cyclic isomers of $[C_4N_{12}]^{\bullet+}$ are either unstable (**I-3**) or much higher in energy (**I-4**). In addition, the formation of structures like **I-4** is unlikely due to high reaction barriers. Thus, the ion at *m*/*z* 216, most likely, has the structure of tetraazidocyclobutadiene. DFT calculations‡ also showed that the further decomposition of the azido groups in this radical cation occurs without the formation of any stable $[C_4N_4]^{\bullet+}$ ions, leading exclusively to $NCCN^{\bullet+}$ and neutral cyanogen.

In summary, a new and very unusual pathway of fragmentations of aromatic azides and 2-cyanopyridines upon electron impact was discovered. The first step of EI induced fragmentation of tetraazidopyridine-2-carbonitrile involves elimination of NCCN to give $[C_4N_{12}]^{\bullet+}$ radical cation. It is therefore not excluded that previously found high rate of the thermal decomposition of tetraazidopyridine-2-carbonitrile is due to the release of NCCN at the initial stages of the thermolysis of this compound. According to DFT calculations, the $[C_4N_{12}]^{\bullet+}$ ion has the structure of tetraazidocyclobutadiene. Although a great variety of substituted cyclobutadienes (ethynyl, cyano, fluoro, chloro, bromo, iodo, *etc*.) and their radical cations have been studied theoretically and experimentally in the last decade,[12] nothing was previously known about azido-substituted cyclobutadienes. Our study demonstrates that these compounds may be experimentally generated in the form of radical cations from some azidopyridine-2-carbonitriles.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.09.005.

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‡ Experimental EI mass spectrum of compound **1** and details of DFT and CCSD(T) calculations are presented in Online Supplementary Materials.

Received: 20th March 2018; Com. 18/5515