Significance statement

Hydrogen cyanide (HCN) and its isomer hydrogen isocyanide (HNC) are prevalent in the interstellar medium (ISM). The ratio between the two isomers serves as an indicator of the physical conditions in different areas of the ISM. As such, the isomerization process between HCN and HNC has been extensively studied on the neutral potential energy surface. Here we demonstrate, for the first time, that the isomerization process can take place on the cationic surface as a result of proton transfer and networks formed by hydrogen bonding. We also discuss the crucial effect the environment has on the isomerization processes. Moreover, we report the formation of structures with high astrobiological relevance upon ionization of the clusters. Understanding the isomerization processes and the chemistry of the clusters are key findings that we believe will be of interest to the scientific community in several fields, including chemistry, astronomy and astrobiology.