A laser ablation method has been successfully used to vaporize the bioactive amino monosaccharide D-glucosamine. Three cyclic $\alpha$-$^{4}$C$_{1}$ pyranose forms have been identified using a combination of CP-FTMW and LA-MB-FTMW spectroscopy. Stereoelectronic hyperconjugative factors, like those associated with anomic or gauche effects, as well as the cooperative OH···O, OH···N and NH···O chains, extended along the entire molecule, are the main factors driving the conformational behavior. All observed conformers exhibit a counter-clockwise arrangement (cc) of the network of intramolecular hydrogen bonds. The results are compared with those recently obtained for D-glucose.\footnote{J. L. Alonso, M. A. Lozoya, I. Peña, J. C. López, C. Cabezas, S. Mata, S. Blanco, Chem. Sci. \textbf{2014}, \emph{5}, 515.}