The pure rotational spectrum of cis-cis peroxynitrous acid, HOONO, has been observed for the first time. Over 220 transitions, sampling states up to $J = 67$ and $K_a = 31$, have been fitted with an RMS uncertainty of 48.4 kHz. The experimentally determined rotational constants agree well with ab initio values for the cis-cis conformer, a five-membered ring formed by intramolecular hydrogen bonding. The small, positive inertial defect, $\Delta = 0.075667(60)\text{amu}\cdot\text{Å}^2$, and lack of any observable torsional splittings in the spectrum indicate that cis-cis HOONO exists in a well-defined planar structure at room temperature. Analysis of the rotational spectrum of the deuterated isotopologue, DOONO, confirms the planar molecular structure and yields substitution coordinates for the hydrogen atom.