To investigate the temperature effect on microscopic hydration structures in clusters, we have recorded ultraviolet photodissociation spectra of hydrated phenol cation, [PhOH(H$_2$O)$_5$]$^+$, under the temperature-controlled condition. The temperature dependence in the spectra clearly exhibits that there are two isomers in the present experimental condition and that the relative populations between them changes with an elevation of the temperature. Among many optimized structures obtained by the DFT calculations, two distinct hydration motifs, ring-with-tail and chain type motifs, are assigned for the isomers observed in our experiment. The change in the relative populations based on our observation is quantitatively interpreted by statistical mechanical estimation based on the DFT calculations. A ring with tail type hydration motif is dominant in cold condition, whereas a chain-like motif is dominant in hot condition. Moreover, possible cooling paths from the chain-like to ring-with-tail type motifs are discussed. In the present paper, temperature effects on the structures of the other hydrogen-bonded phenol cation clusters than [PhOH(H$_2$O)$_5$]$^+$ are also introduced.