

Supplementary Information

N-acetylglycine Cation Tautomerization Enabled by the Peptide Bond

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Theoretical details

A detailed study of the potential energy surface (PES) of neutral and singly positively charged N-acetylglycine is presented here. In the following figures we present the critical points (minima and transition states) corresponding to:

- Structure of neutral conformers of N-acetylglycine (Fig. 1);
- Isomerisation pathways for neutral N-acetylglycine conformers (Fig. 2);
- Structure of singly charged conformers of N-acetylglycine (Fig. 3);
- Isomerisation pathways for singly charged N-acetylglycine conformers (Fig. 4);
- Structure of singly charged diols of N-acetylglycine (Fig. 5);
- Isomerisation pathways for singly charged N-acetylglycine diols (Fig. 6).

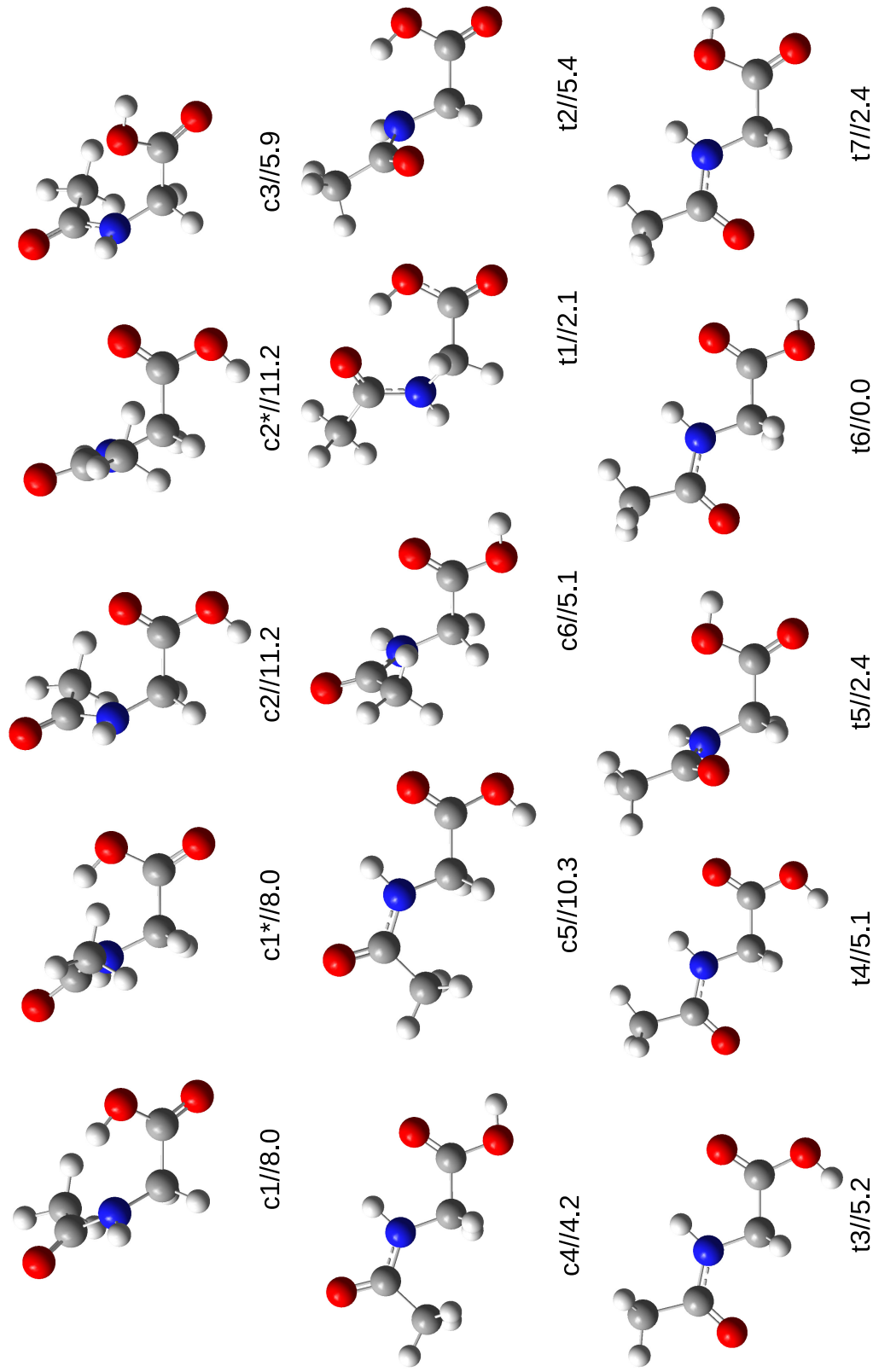


Figure 1: Structure of neutral conformers of N-acetylglycine; “c” (*cis*) and “t” (*trans*) notation underline the position of the atoms with respect to peptide bond; star “*” indicates the rotamers. Relative energies are given in kcal mol⁻¹ at the DFT-B3LYP/6-311++G(d,p) level of theory with respect to the most stable isomer of the neutral molecule (t6) including the zero point energy correction.

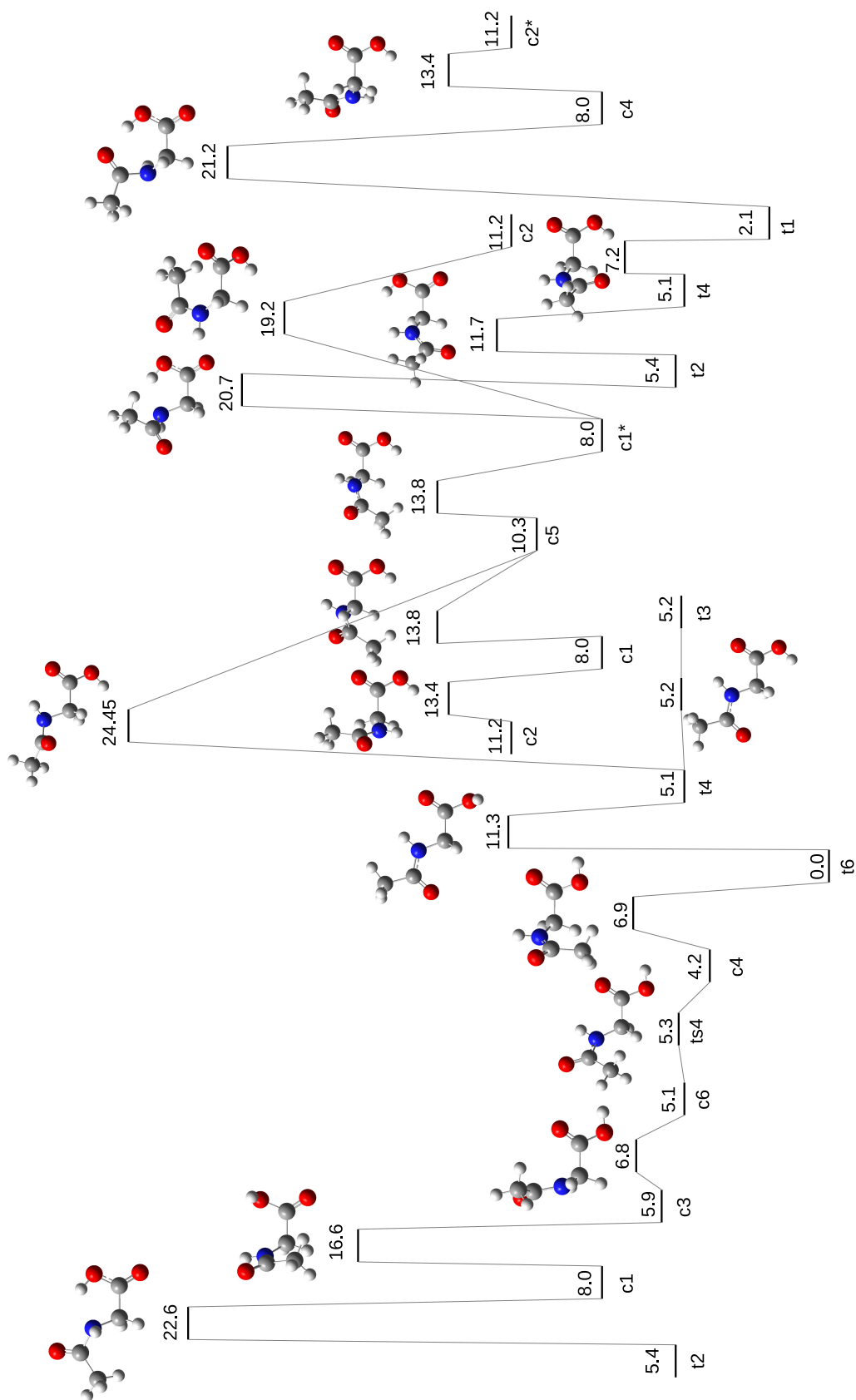


Figure 2: Isomerisation pathways for neutral N-acetylglycine. Relative energies are given in kcal mol⁻¹ with respect to the most stable neutral conformer of N-acetylglycine (t6) at DFT-B3LYP/6-311++G(d,p) level of theory including the zero point energy correction.

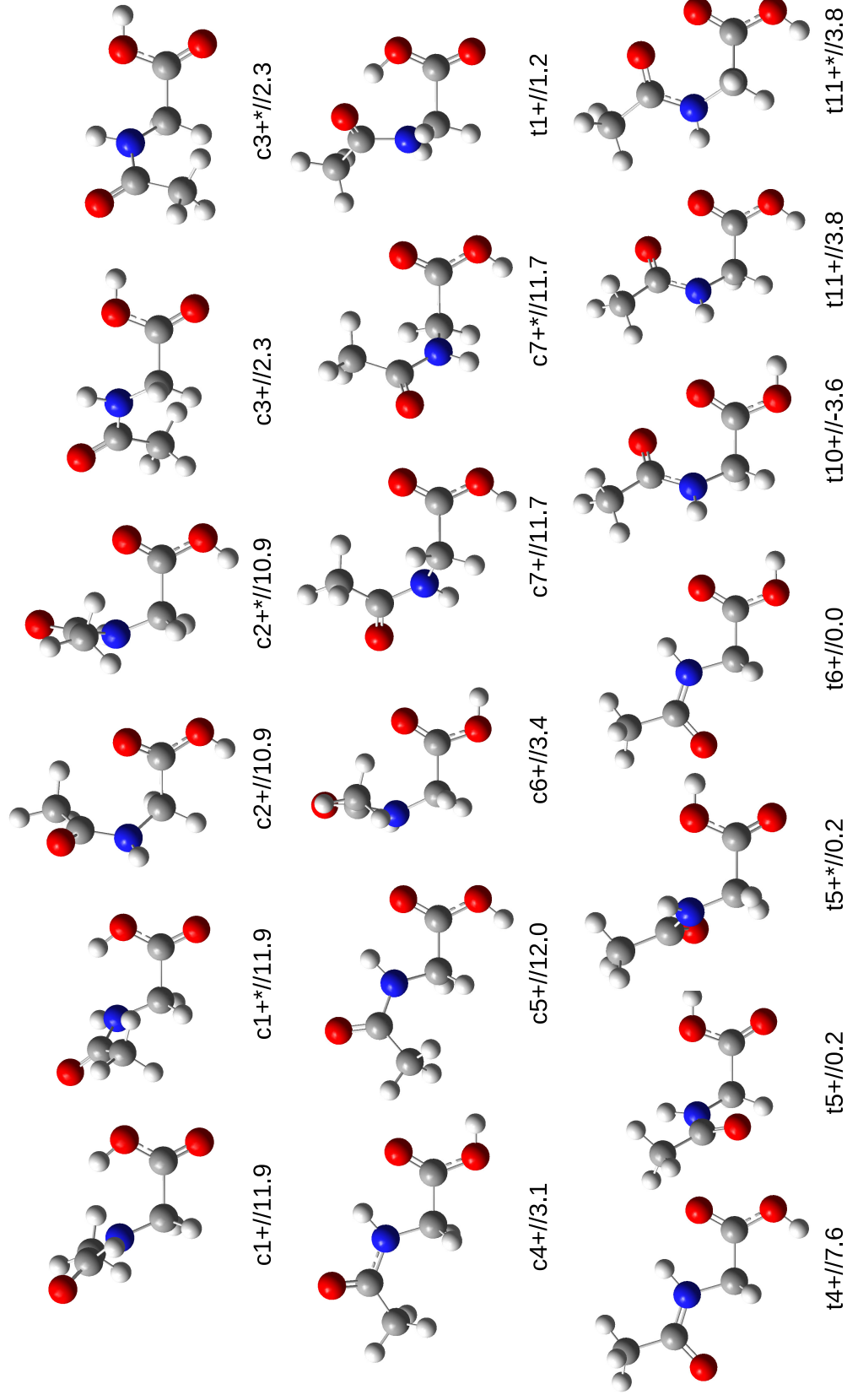


Figure 3: Structure of singly charged conformers of N-acetyllysine; “c” (*cis*) and “t” (*trans*) notation underline the position of the atoms with respect to peptide bond; star “*” indicates the rotamers. Relative energies are given in kcal mol⁻¹ with respect to the t6+ conformer at the DFT-B3LYP/6-311++G(d,p) level of theory including the zero point energy correction.

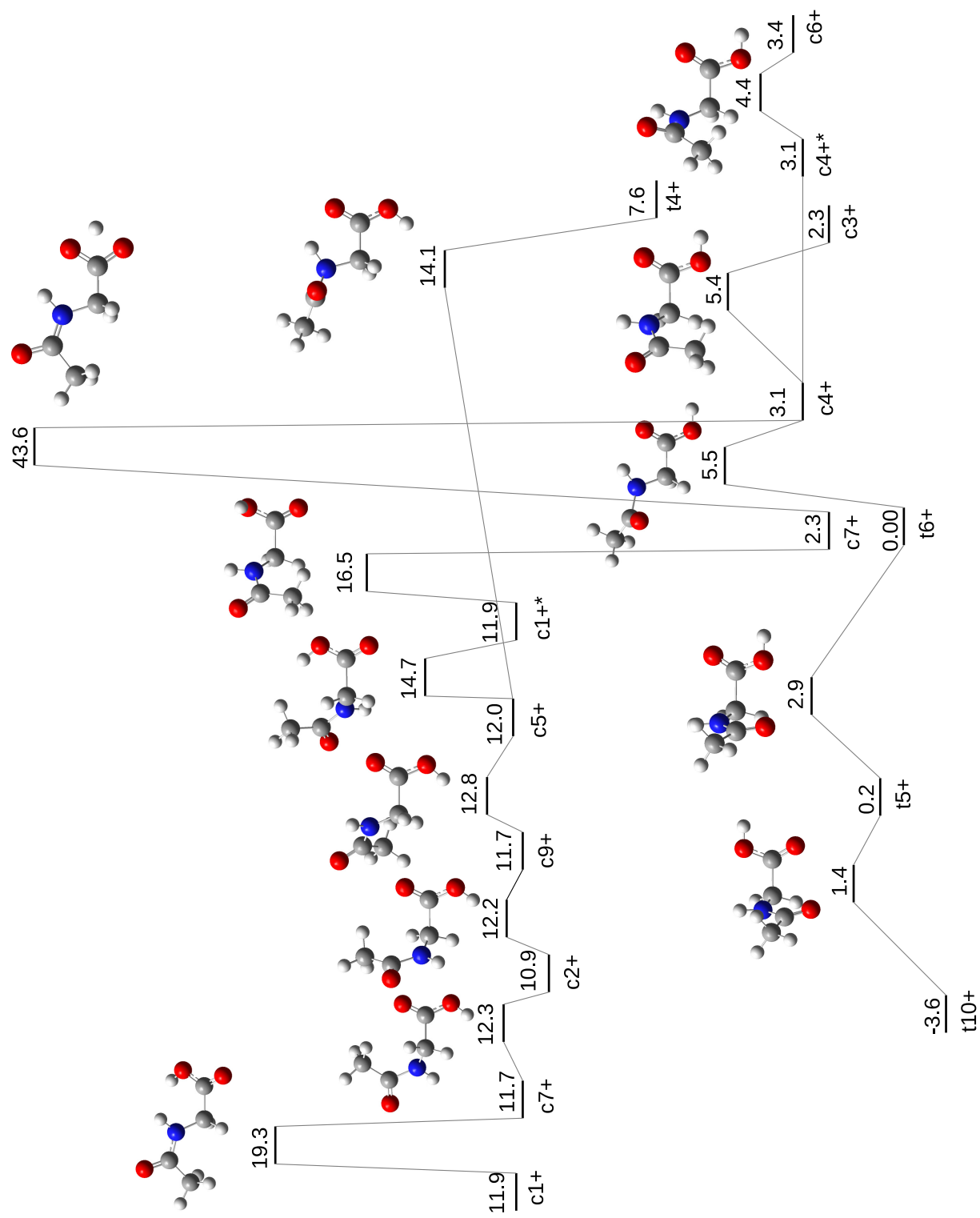


Figure 4: Isomerisation pathways for singly charged N-acetylglycine. Relative energies are given in kcal mol⁻¹ with respect to the t6+ conformer of N-acetylglycine at DFT-B3LYP/6-311++G(d,p) level of theory including the zero point energy correction.

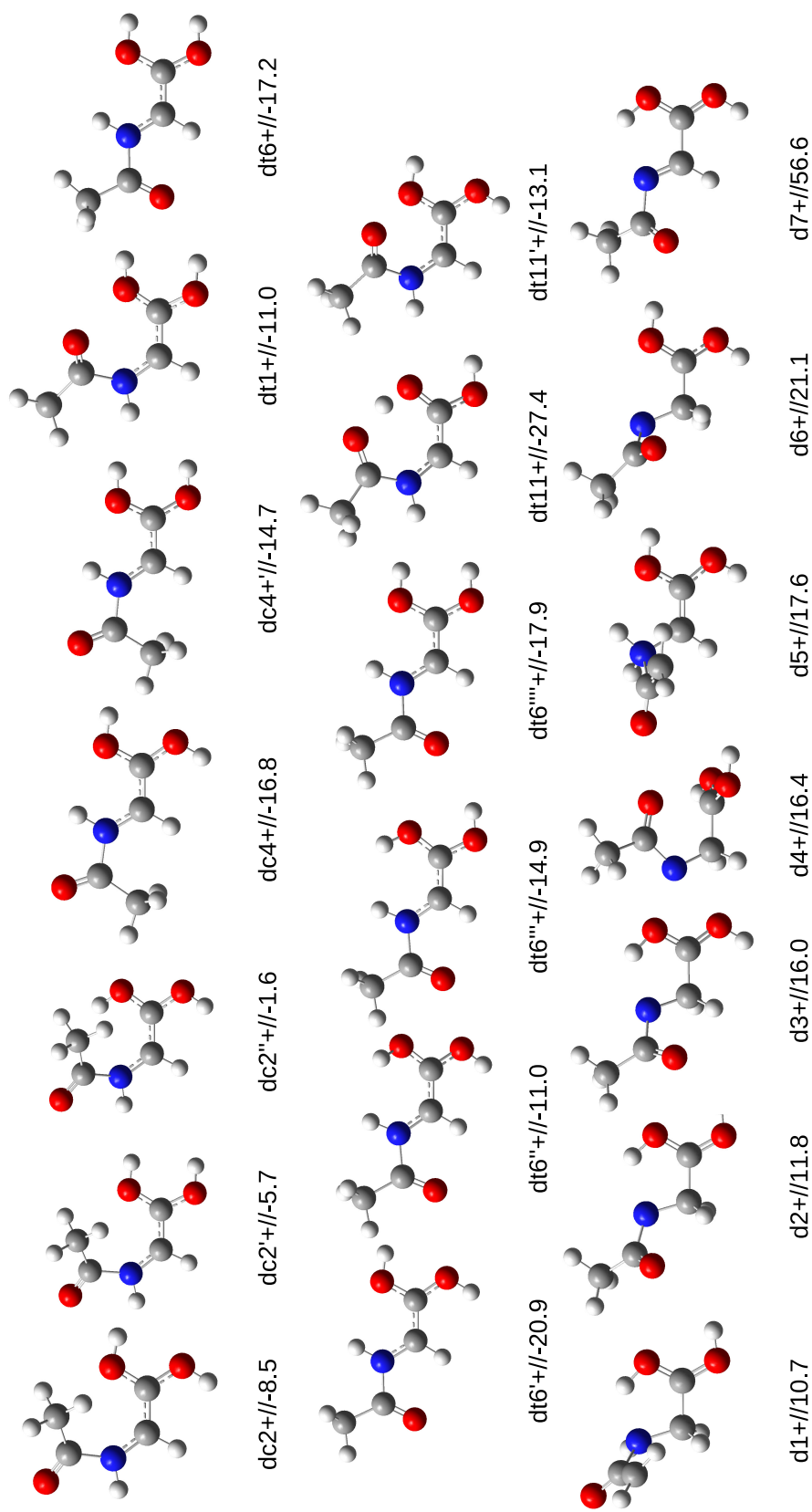


Figure 5: Structure of singly charged diols (d) of N-acetyllysine; “c” (*cis*) and “t” (*trans*) notation underline the position of the atoms with respect to peptide bond; apostrophe ”’” indicates the different relative position of two hydrogens in a geminal diol cations. Relative energies are given in kcal mol⁻¹ with respect to the t6+ conformer at the DFT-B3LYP/6-311++G(d,p) level of theory including the zero point energy correction.

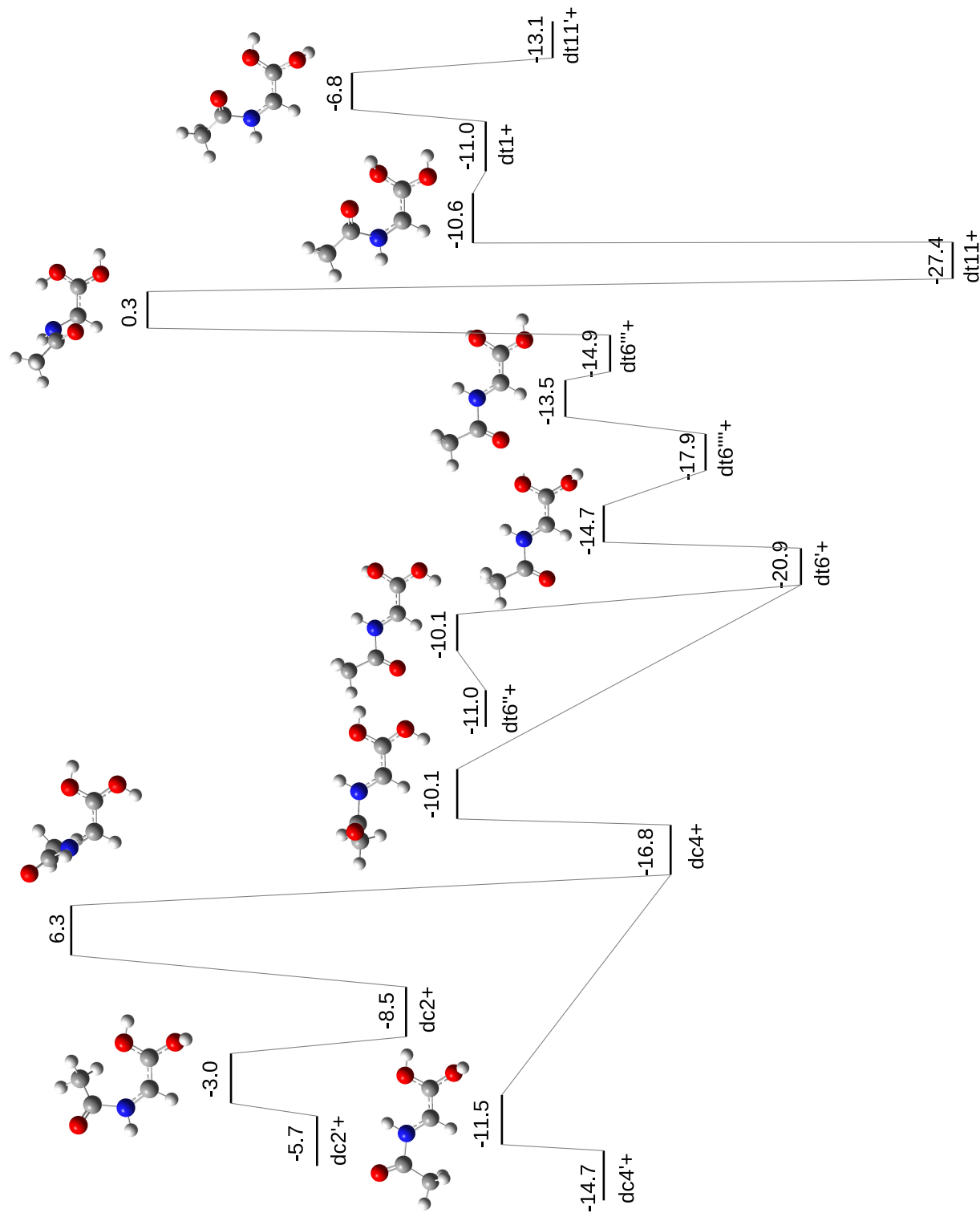


Figure 6: Isomerisation pathways for singly charged N-acetylglycine diols; apostrophe “ ’ ” indicates the different relative position of two hydrogens in a geminal diol cations. Relative energies are given in kcal mol⁻¹ with respect to the t6+ conformer of N-acetylglycine at DFT-B3LYP/6-311++G(d,p) level of theory including the zero point energy correction.