Conformational Phase Transitions Associated with Reversal of Hydrogen Bond Direction in 4-Chloro- and 4-Bromobenzyl Alcohols. An X-Ray Study

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Notable changes in the molecular conformations of 4-chlorobenzyl alcohol around the $C(H_2)$-C_{ar} and O-$C(H_2)$ bonds were found to take place at the first-order phase transition point (T_{c1} = 236 K). Quite similar phenomena were observed at T_{c1} (217 K) of the isomorphic 4-bromo compound. The two kinds of conformational changes are considered to couple and cause the reversal of the direction of the linear O-H…O hydrogen bond as the compound undergoes the first-order transition. The CH_2OH moiety participates in several short intermolecular contacts, and a C-H…π interaction exists between the CH_2 and the neighboring phenyl group. These intermolecular factors seem to contribute to the regulation of the molecular conformation in the crystal. The C-O bond length of each compound shortens considerably at $T > T_{c1}$.

Key words: Crystal Structure; Phase Transition; Hydrogen Bond; Molecular Conformation.