

^2H NMR Study on Phase Transitions and Crystal Dynamics of *p*-Chloro- and *p*-Bromobenzyl Alcohols

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Z. Naturforsch. **57 a**, 388–394 (2002); received January 23, 2002

Presented at the XVth International Symposium on Nuclear Quadrupole Interactions, Hiroshima, Japan, September 9-14, 2001.

Two phase transitions of 4-chlorobenzyl alcohol (*p*CBA) and 4-bromobenzyl alcohol (*p*BBA), from the low-temperature phase (LTP) to the intermediate-temperature phase (ITP) and from ITP to the room-temperature phase (RTP), were investigated by ^2H NMR and differential scanning calorimetry (DSC). The crystal dynamics in each phase were studied using the ^2H NMR spectra, the spin-lattice relaxation time (T_1) and the relaxation time of quadrupole order (T_{1Q}) for the samples, where the hydrogen of the -OH group was selectively deuterated. The ^2H NMR T_1 of both crystals in the RTP were dominated by the fluctuation of the electric field gradient at ^2H nucleus caused by vibrational motions of the -CH₂OH group. In the LTP of both crystals, the fast jump of hydrogen atoms between the two sites corresponding approximately to the positions of the hydroxyl hydrogen atoms in the RTP and LTP were found from ^2H NMR spectra. The results of T_1 and T_{1Q} in the LTP revealed that the jump of hydrogen atoms occurs in asymmetric potential wells and that these potential wells gradually approach symmetric ones with increasing temperature on the high-temperature side in the LTP.

Key words: Crystal Structure; Phase Transition; ^2H NMR; Crystal Dynamics; Hydrogen Bond.