Abstract: The effect of fluorination on the conformational and hydrogen-bond (HB)-donating properties of a series of benzyl alcohols has been investigated experimentally by IR spectroscopy and theoretically with quantum chemical methods (ab initio (MP2) and DFT (MPWB1K)). It was found that o-fluorination generally resulted in an increase in the HB acidity of the hydroxyl group, whereas a decrease was observed upon o,o'-difluorination. Computational analysis showed that the conformational landscapes of the title compounds are strongly influenced by the presence of o-fluorine atoms. Intramolecular interaction descriptors based on AIM, NCI and NBO analyses reveal that, in addition to an intramolecular OH···F interaction, secondary CH···F and/or CH···O interactions also occur, contributing to the stabilisation of the various conformations, and influencing the overall HB properties of the alcohol group. The benzyl alcohol HB-donating capacity trends are properly described by an electrostatic potential based descriptor calculated at the MPWB1K/6-31+ G(d,p) level of theory, provided solvation effects are taken into account for these flexible HB donors.