Abstract: Rational modulations of molecular interactions are of significant importance in compound properties optimization. We have previously shown that fluorinationofconformationally rigid cyclohexanols leads to attenuation of their hydrogen-bond (H-bond) donatingcapacity (designated by pKAHY)when OH···F intramolecular hydrogen-bond (IMHB) interactions occur,asopposed to an increase in pKAHY due to the fluorine electronegativity.This work has now been extended to awider range of aliphatic b-fluorohydrins with increasing degrees of conformational flexibility.Weshow that the observed differences in pKAHY between closely related diastereomers can be fully rationalized by subtle variations in populations of conformers able to engage in OH···F IMHB, as well as by the strength of these IMHBs. We also show that the Kenny theoretical Va(r) descriptor of H-bond acidity accurately reflects the observed variations and acalibration equationextended to fluorohydrins is proposed.This work clearlyunderlines the importance of the weak OH···F IMHB in the modulation of alcohol H-bond donating capacity.