

TIPPING THE BALANCE BETWEEN ELECTROSTATICS AND STERIC EFFECTS: THE MICROWAVE SPECTRA AND MOLECULAR STRUCTURES OF 2-CHLORO-1,1-DIFLUOROETHYLENE-ACETYLENE AND *CIS*-1,2-DIFLUOROETHYLENE-ACETYLENE

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We have found that the observed average structures of haloethylene-protic acid heterodimers result from an interplay between favorable electrostatic interactions and steric effects. For vinyl fluoride and 1,1-difluoroethylene complexes, steric effects predominate and the acid binds across the double bond (“top”), while for trifluoroethylene, favorable electrostatics forces the complexes to adopt a sterically strained structure with the acid at one end of the olefin (“side”). A relaxation of steric requirements for binding with a chlorine atom leads to different geometries being observed for each of the vinyl chloride complexes with hydrogen fluoride, hydrogen chloride, and acetylene. The side binding motif to chlorine persists in (*Z*)-1-chloro-2-fluoroethylene-acetylene despite the presence of the more electronegative fluorine atom. For 2-chloro-1,1-difluoroethylene ethylene-acetylene, the acetylene is presented with the option of top binding to fluorine versus side binding to chlorine, whereas with *cis*-1,2-difluoroethylene, the only option is side binding to fluorine. The structures of these two complexes are compared to reveal the balance between electrostatics and sterics.