HALOGEN BONDS AND HYDROGEN BONDS IN THE GAS PHASE: SIMILARITY REVEALED THROUGH ROTATIONAL SPECTROSCOPY.

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Many hydrogen-bonded species B···HX, where B is a simple Lewis base and X is halogen atom, were extensively investigated by rotational spectroscopy in the 1980/90's to yield various properties of the isolated complexes. Systematic variation of B, and then X, allowed generalisations concerned with the hydrogen bond to be identified. More recent examinations of several series of complexes B···XY, where XY is either a homo- or hetero-dihalogen molecule, have revealed striking parallelisms between the properties of the B···XY and those of their hydrogen-bonded counterparts B···HX, thereby suggesting that the generalisations made for the hydrogen-bonded series also apply to B···XY. Accordingly, the weak intermolecular bond in B···XY has been called a halogen bond. Here, attention will focus mainly on angular geometry for selected pairs B···HCl and B···ClF. It will be shown that B···HCl and B···ClF are essentially isomorphous for a given B, but with the hydrogen bond exhibiting a greater propensity to be non-linear. To test the effect that weakening the hydrogen bond has on its deviation from linearity, reference will be made to some complexes B···HCCH in which ethyne is the H-atom donor.