The nature of improper, blue-shifting hydrogen bonding verified experimentally.

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Streszczenie

In the infrared spectra of solutions in liquid argon of dimethyl ether ($(CH_3)_2O$) and fluoroform (HCF_3), bands due to a 1:1 complex between these monomers have been observed. The C−H stretch of the HCF_3 moiety in the complex appears 17.7 cm^{-1} above that in the monomer, and its intensity decreases by a factor of 11(2). These characteristics situate the interaction between the monomers in the realm of improper, blue-shifting hydrogen bonding. The complexation shifts the C−F stretches downward by some 9 cm^{-1}, while the C−H stretches in $(CH_3)_2O$ are shifted upward by 9−15 cm^{-1}, and the C−O stretches are shifted downward by 5 cm^{-1}. These shifts are in very good agreement with those calculated by means of correlated ab initio methods, and this validates a two-step mechanism for improper, blue-shifting hydrogen bonding. In the first step, the electron density is transferred from the oxygen lone electron pairs of the proton acceptor ($(CH_3)_2O$) to fluorine lone electron pairs of the proton donor (CHF_3) which yields elongation of all CF bonds. Elongation of CF bonds is followed (in the second step) by structural reorganization of the CHF_3 moiety, which leads to the contraction of the CH bond. It is thus clearly demonstrated that not only the spectral manifestation of H-bonding and improper H-bonding but also their nature differ.

Słowa kluczowe

Deformation, Electron density, Monomers, Noncovalent interactions, Stabilization

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