WEAK C-H···O AND C-H···F HYDROGEN BONDS IN THE TRIFLUOROMETHANE···OXIRANE AND DIFLUOROMETHANE···OXIRANE COMPLEXES

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Alkanes appear capable of forming hydrogen bonds when sufficiently activated by neighboring electronegative substituents. In this context, the C-H···O interaction between the substituted alkanes trifluoromethane and difluoromethane with oxirane has been analyzed by molecular beam Fourier transform microwave spectroscopy. The ground state rotational spectra of $C_2H_4O\cdots HCF_3$, $^{13}CCH_4O\cdots HCF_3$, $C_2H_4O\cdots H^{13}CF_3$, $C_2H_4O\cdots H_2CF_2$, $C_2H_4O\cdots H_2^{13}CF_2$ and $^{13}CCH_4O\cdots H_2CF_2$ isotopomers have been studied, in their natural abundances, in the frequency range 6-18 GHz. A C_s symmetry has been established for the oxirane···trifluoromethane complex with the C-H bond of trifluoromethane pointing to the domain of the nonbonding electron pairs of the O atom. The cooperative effect of two C-F···H-C interactions increases the stability of the complex. The barrier to internal rotation of the CF_3 group has been determined from the observed A-E splittings. In the oxirane···difluoromethane complex the determined structural data reveals the existence of two bifurcated hydrogen bonds: one between the CH_2 group of difluoromethane with the O atom of oxirane and the other between the methylenic C-H groups of oxirane with the closest fluorine atom of difluoromethane. To our knowledge this is the first experimental evidence of this behaviour. The C-H···S interaction has been also analyzed in the trifluoromethane···tiirane complex. The rotational spectra of $C_2H_4S\cdots HCF_3$, $C_2H_4^{34}S\cdots HCF_3$, $^{13}CCH_4S\cdots HCF_3$ and $C_2H_4S\cdots H^{13}CF_3$ isotopic species have been studied in their natural abundance.