Halogen-Bonded Complexes (XBCs) in Solution: A Spectroscopic and DFT Study

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Halogen bonding (XB) refers to interactions of halogen atoms with electron-rich compounds, leading to the formation of XB complexes (XBCs).[1] Recently, XBCs have played a substantial role in inducing photochemical organic reactions.[2] In this work,[3] we study the formation of XBCs between tertiary amines and CBr_4 in solution, employing DFT, TDA-DFT (Tamm-Dancoff approximation), UV-Vis, and NMR studies, in order to understand the ability of XBCs generation. It is known that the formation of a XBC can be observed via UV-Vis spectroscopy by the appearance of a new band shifted to higher wavelengths, upon mixing the two components.[4] However, no systematic study of XBC generation between tertiary amines and CBr_4, using ^{13}C NMR spectroscopy has been conducted so far. ^{13}C NMR spectra of a solution of CBr_4 alone and the corresponding mixtures of CBr_4-amine were recorded, indicating clear shifts for the CBr_4 carbon atom. Additionally, ^{13}C NMR studies were performed in order to determine the association constant of some of the studied XBCs. Furthermore, DFT and TDA-DFT studies were performed in ACN to calculate the binding energies, the involved S_0 and T_1 states and their properties and their theoretical UV-Vis spectra. Lastly, DFT and UV-Vis studies were carried out for the case of DABCO with different halomethanes, in order to determine if CBr_4 is a better XB donor. The XBC generation concept was implemented for the light-mediated amide formation. According to the acquired results, all tertiary amines may form halogen bonds with CBr_4, however the properties of such a bond seem to vary.

References:

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