

σ -hole interaction properties of divalent sulfur

Albert Singa Lundemba

University of Kinshasa, Kinshasa, Democratic Republic of the Congo

albert.lundemba@unikin.ac.cd

Non-covalent interactions like hydrogen bonds, aromatic stacking contacts and even σ -hole interactions are commonly observed in biologic macromolecular compounds like proteins, polysaccharides, and nucleic acids. These rather weak interactions often play a significant role in determining the tertiary structure of macromolecules. Evidence of σ -hole interactions has been given by both theoretical and experimental studies reported in the literature. The present study explores the σ -hole interaction properties of divalent sulfur groups (R_1 -S- R_2) using the Cambridge Structural Database (CSD) in conjunction with *ab initio* calculations. CSD analysis revealed that

7 095 structures contained a divalent sulfur atom that formed an intermolecular σ -hole contact within the sum of the van der Waals radii with N, O, F, P, S, Cl, As, Se, Br, Sb, Te or I as the acceptor atom. The structural fragments (C,C)-S, (C,S)-S, (N,S)-S, (C,N)-S, (N,N)-S, (S,S)-S, (C,Se)-S, (C,P)-S, (C,Te)-S and (C,As)-S were each observed to exhibit intermolecular contacts that are potentially σ -hole interactions. The geometric preferences of some of these contacts indicated that genuine σ -hole interactions were likely. That finding was confirmed by the geometries of the optimised complexes formed by the σ -hole donors $CH_3O-S-OCH_3$ (KUYRIF), FOCS-CN (AMOREA), $(CH_3)_2N-S-Cl$ (VAMPEF) and CN-S-CN (fragment of GOJZUC) derived from the CSD. Values of the binding energy (BE) calculated with B3LYP were markedly smaller than values calculated with MP2, the latter being close to those with B3LYPD3-G and B3LYPD3-BJ. This suggested that dispersion interactions were in addition to σ -hole interactions the main forces stabilizing the complexes. The energy of the σ -hole interaction was dependent on the environment of the sulfur atom. The dependence agreed well with molecular electrostatic potential surfaces of the donors and partial charges of the sulfur atom predicted by *ab initio* calculations. The positive charge of the sulfur atom was enhanced when increasing the electron withdrawing effect of the substituents R_1 and R_2 in the following sequence: $F > CH_3O > CN > Cl > Br$.

Keywords: sigma-hole, CSD, DFT