

Comparison of lithium and hydrogen bonds in $(X\cdots Li\cdots X)^-$ and $(X\cdots H\cdots X)^-$ ($X=F, Cl$ and Br) complexes: topological analysis of electron localization function.

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Streszczenie

The topological analysis of the electron localization function (ELF) is used to elucidate the nature of the hydrogen and lithium bonds in the $(X\cdots Y\cdots X)^-$ ($X|F, Cl, Br; Y|H, Li$) complexes. The lithium bond that exhibits an electrostatic nature is characterized by a constant mean electron population of the lithium core basin $C(Li)$ equal to $2.03e$. The values of the ELF within $Li\cdots X$ regions are smaller than 0.5 corresponding to a totally delocalized electron density. For the $X\cdots H$ hydrogen bonds a covalent nature is found with an essential electron pairing, as implied by values of ELF in the $H\cdots X$ regions larger than 0.5. The mean electron population of the $V(H)$ basin depends on electronegativity of a halogen atom, and it ranges from $0.17e$ for $(F\cdots H\cdots F)^-$ to $2.11e$ for $(Br\cdots H\cdots Br)^-$. The polarization of halogen anions X^- by lithium or hydrogen cations results in an anisotropy of the nonbonding electron density, which is reflected by two valence attractors $V_1(X_{i=1,2})$ and $V_2(X_{i=1,2})$ found inside and outside a complex, respectively. The analysis of the $H\cdots Br$ hydrogen bond reveals essential differences as compared with the $H\cdots X$ ($X|F$ and Cl) hydrogen bonds. The topology of nonbonding electrons of Br yields only one valence, monosynaptic basin $V(Br_{i=1,2})$. Furthermore, similarity of the $H\cdots Br$ hydrogen bonds to a bond in an isolated HBr molecule is noted. The increased Pauli repulsion between the $V(H)$ and $V_1(X_{i=1,2})$ basins in the $(X\cdots H\cdots X)^-$ complexes leads to a larger electron delocalization of $V_1(X_{i=1,2})$ as compared with the $(X\cdots Li\cdots X)^-$ systems.

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