

X₂Y₂ Isomers: Tuning Structure and Relative Stability through Electronegativity Differences

(X = H, Li, Na, F, Cl, Br, I; Y = O, S, Se, Te)

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ABSTRACT

We have studied the XXXX and X₂YY isomers of the X₂Y₂ species (X = H, Li, Na, F, Cl, Br, I; Y = O, S, Se, Te) using Density Functional Theory at the ZORA-BP86/QZ4P level. Our computations show that over the entire range of our model systems the XXXX isomers are more stable than the X₂YY forms except for X = F and Y = S and Te, for which the F₂SS and F₂TeTe isomers are slightly more stable. Our results also point out that the Y–Y bond length can be tuned quite generally through the X–Y electronegativity difference. The mechanism behind this electronic tuning is the population or depopulation of the π* in the YY fragment.

KEYWORDS: Bond theory, Density functional calculations, Energy decomposition analysis, Dichalcogenides, Peroxides, Disulfides.