

# On the use of energy decomposition analyses to unravel the origin of the relative stabilities of isomers

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## Abstract

Over the past decades, the stability of the isomers and the nature of the chemical bond have attracted considerable attention since many of these species intervene in industrial, biochemical, and atmospheric processes. The understanding of the relative stabilities of these species has not been fully achieved yet and, moreover, some thermochemical data is still missing. For this purpose, we decided to use the DFT calculations to unravel the origin of the relative stabilities of isomers in four different projects.

The first study discusses the isomerization energies of 1,2-/1,3-diazacyclobutadiene, pyrazole/imidazole, and pyridazine/pyrimidine with the turn-upside-down approach. This research project aimed to provide a better comprehension on the origin of the NN bond destabilization. In this study, it was found that, in the three cases, the higher stability of the 1,3-isomers is not due to lower Pauli repulsions but because of the more favorable  $\sigma$ -orbital interactions involved in the formation of two C–N bonds in comparison with the generation of C–C and N–N bonds in the 1,2-isomers.

In the second study, we have studied the XYYX and X<sub>2</sub>YY isomers of the X<sub>2</sub>Y<sub>2</sub> species (X = H, Li, Na, F, Cl, Br, I; Y = O, S, Se, Te) using DFT at the ZORA-BP86/QZ4P level. Our computations show that, over the entire range of our model systems, the XYYX isomers are more stable than the X<sub>2</sub>YY forms except for X = F and Y = S and Te, for which the F<sub>2</sub>SS and F<sub>2</sub>TeTe 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  $\pi^*$  in the YY fragment.

Then, we have made a comparison between alkalimetal ( $M = \text{Li, Na, K, and Rb}$ ) and group 11 transition metal ( $M = \text{Cu, Ag, and Au}$ )  $(MX)_4$  tetramers with  $X = \text{H, F, Cl, Br, and I}$  has been carried out by means of the Amsterdam Density Functional software using DFT at the BP86/QZ4P level of theory and including relativistic effects through the ZORA approximation. We have obtained that, in the case of alkalimetals, the cubic isomer of  $T_d$  geometry is more stable than the ring structure with  $D_{4h}$  symmetry, whereas in the case of group 11 transition metal tetramers, the isomer with  $D_{4h}$  symmetry (or  $D_{2d}$  symmetry) is more stable than the  $T_d$  form. To better understand the results obtained we have made energy decomposition analyses of the tetramerization energies. The results show that in alkalimetal halide and hydride tetramers, the cubic geometry is the most stable because the larger Pauli repulsion energies are compensated by the attractive electrostatic and orbital interaction terms. In the case of group 11 transition metal tetramers, the  $D_{4h}/D_{2d}$  geometry is more stable than the  $T_d$  one due to the reduction of electrostatic stabilization and the dominant effect of the Pauli repulsion.

And the last part is based on an analysis of the relative stabilities of ortho, meta, and para  $MClY(XC_4H_4)(PH_3)_2$  heterometallabenzenes ( $M = \text{Rh, Ir; X = N, P; Y = Cl}$  and  $M = \text{Ru, Os; X = N, P; Y = CO}$ ). The results show that the meta isomer is the most stable for  $X = \text{N}$  and  $M = \text{Ir, Rh}$ , the ortho is the lowest-lying isomer for  $X = \text{P}$  irrespective of the metal, and for  $X = \text{N}$  and  $M = \text{Ru, Os}$ , the ortho and meta isomers are almost degenerate. The electronic structure and bonding situation have been investigated with energy decomposition analyses of the interaction energy between various fragments to discuss the origin of the differences observed.