

*Halogen...halogen interactions in the light of geometrical correction*

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Halogen...halogen interaction is one of the most discussed topics among supramolecular interactions. The nature of the interactions is still a matter of debate. Due to weak nature of the interactions and high atomic weights of the heavier halogens, there are several difficulties encountered in the experimental as well as theoretical methods of studies and understanding these interactions convincingly. Therefore, statistical analysis has become an interesting tool to study these interactions. Though geometrical correction, namely cone correction, has been used in the case of statistical analysis of hydrogen bonds, interestingly, no such attempt has been made for the halogen...halogen interactions. Without geometrical corrections, conclusions drawn from the statistical analysis so far have been erroneous. Here, new geometrical corrections have been introduced and applied to the statistical analysis of halogen...halogen interactions which reveals several new interesting features in these interactions.

There are several interesting and significant differences found between the outcomes of statistical analysis without geometrical correction and after geometrical corrections. i) The most interesting difference is found in C-F...F-C interactions. The statistical analysis of C-F...F-C interactions without geometrical correction shows a preferences for lower  $\Delta\theta$ , whereas the % population as expected, after geometrical corrections, is almost flat. It implies that F does not have much preference for any  $\Delta\theta$ . ii) The minima, separating the Type 1 (lower  $\Delta\theta$ ) and Type 2 (higher  $\Delta\theta$ ) geometries at  $\Delta\theta = 10-20^\circ$  range, are much deeper and the % population at higher  $\Delta\theta$  (Type 2 interactions) are more prominent after geometrical corrections. iii) The maxima at Type 2 region are shifted by 20 to 30° towards the  $\Delta\theta = 90^\circ$  (an ideal geometry for Type 2 interaction) compared to that found in the uncorrected plot of population vs.  $\Delta\theta$ . iv) Statistical analysis without geometrical correction shows a dominance of Type 1 interactions whereas, statistical analysis after geometrical correction shows a reverse trend in Cl, Br and I. vi) Shape correction on C-I...I-C interactions reveals that these interactions are highly directional in comparison to what was known so far without geometrical corrections.

The geometrical corrections used here is more general and hence can be used in several other interactions. We anticipate that this study would be able to modify the concept about the nature of halogen...halogen interactions and this method of geometrical corrections would be applied to many other interactions.

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