A New Type of Halogen–Halogen Bonds

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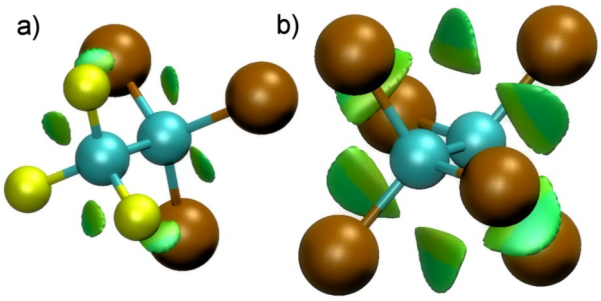
Abstract

The interactions between the two CX_3 groups in perhalogenated ethanes, $X_3C–CX_3$ are studied, with $X_3C–CX_3$ = $H_3C–CH_3$, $F_3C–CF_3$, $F_3C–CCl_3$, and $Cl_3C–CCl_3$. Utilising the recently developed method for revealing non-covalent interactions in molecular systems by Johnson *et al*. [1], a previously overlooked non-covalent interaction between halogens attached to opposite carbon atoms is unearthed. Further insight is obtained by means of the Salvador–Mayer energy component analysis [2] accompanied by a plethora of other abstract concepts.



Quantum chemical calculations extrapolated towards the full solution of the Schrödinger equation reveal the complex nature of this attractive interaction. When at least one of the halogens is a chlorine, the strength of the interaction is comparable to that of hydrogen bonds. The bond character is quite different from standard non-covalent halogen bonds and hydrogen bonds; no bond critical points are found between the halogens, and the σ-holes of the halogens are not utilised for bonding. Thus, the nature of the halogen···halogen interaction studied here appears to be of an unusually strong van der Waals type, and apparently rather controversial [3].

References

[1] E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen, W. Yang, "Revealing Non-Covalent Interactions", *J. Am. Chem. Soc.* **132** (2010) 6498.

[2] P. Salvador, I. Mayer, "One- and two-center physical space partitioning of the energy in the density functional theory", *J. Chem. Phys.* **126** (2007) 234113.

[3] M. P. Johansson, M. Swart, "Intramolecular Halogen–Halogen Bonds" (submitted, several times)