The *N*-methylammonium moiety: A tetrel bond donor site

A. Daolio[1], E. K. Wieduwilt[2], G. Terraneo[1], A. Genoni[2], G. Resnati[1]

[1] NFMLab - Department of Chemistry, Materials and Chemical Engineering "Giulio Natta", Politecnico di Milano, Via L. Mancinelli 7, I-20131 Milan, Italy.
[2]Université de Lorraine, Laboratoire SRSMC, UMR 7565, Vandoeuvre-lès-Nancy, F-54506, France.

andrea.daolio@polimi.it

A σ-hole interaction can be defined as a net attractive interaction between an area of positive electrostatic potential generated on the outer surface of an atom by one of the covalent σ-bonds it is involved in and an electron rich site (Lewis base, e.g., a lone-pair possessing atom or an anion) in the same or another molecular entity. According to the formalism of naming these interactions from the group of the periodic table the atom bearing the σ-hole belongs to [1], an interaction between a Lewis base and an atom of the Group 14 functioning as the electrophilic site is dubbed Tetrel Bond (TtB).

The *N*-methylammonium residue is ubiquitous in biology and chemistry, and many *N*-methylammonium bearing compounds are often used in crystal engineering for the designed formation of crystal architectures [2].

We propose here a series of 1,6-bis-trimethylammonium hexane crystal structures displaying a close contact between one carbon atom of an *N*-methylammonium moiety and a neutral and lone-pair-possessing atom or an anion. The geometrical features of these interactions are those typical for a TtB (i.e., linearity of the N^{+}–C···electron-rich site angle, distance between C and the electron-rich site shorter than the sum of VdW radii of involved atoms) and are maintained when both charged and neutral species approach the *N*-methylammonium carbon [3].

Hirschfeld Atom Refinement (HAR) and Atom In Molecules (AIM) computational analyses have also been carried out to asses if the interaction occurring in the crystal packing between the *N*-methylammonium moiety and the electron rich sites are in fact hydrogen bonds (HB) or TtBs. The latter hypothesis is indeed confirmed by these analyses.

In conclusion, the reported experimental and theoretic results indicate that the close contacts between the carbon atom of an *N*-methylammonium residue and an electron-rich site are TtBs and that the interaction can be robust enough to be employed as an additional tool in the design of crystalline architectures involving this moiety. It can be expected the interaction plays a role in driving or influencing recognition processes involving biomolecules containing the *N*-methylammonium residue.

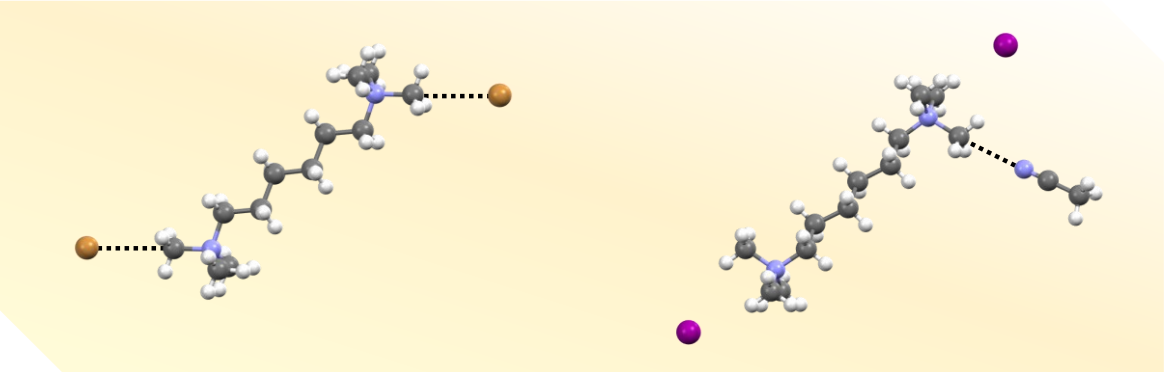

Figure 1. Ball and stick representation (Mercury) of two structures wherein the electron-rich site is an anion (left) and a neutral and lone-pair possessing atom (right). TtBs are black dotted lines.

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