

## MS30- Halogen and chalcogen bonding in the solid state

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### MS30-P01

#### Cl ... Cl halogen bonds and N-oxide ... N-oxide interactions in crystal structure of pentachloropyridine N-oxide

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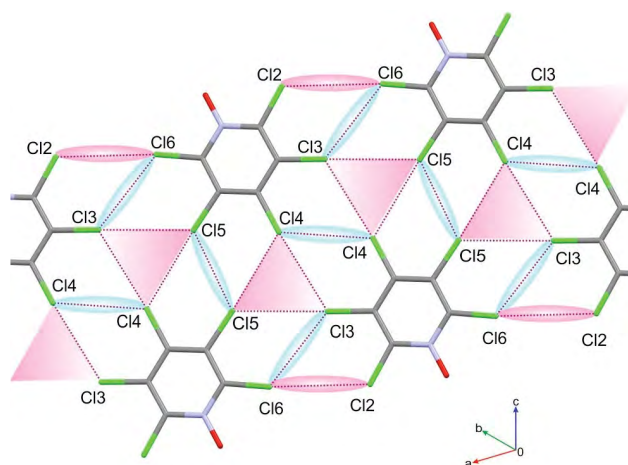
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In comparison with other halogens, fluorine and chlorine atoms are present in a large number of active compounds of chemical and biological importance. However, fluorine in contrast to chlorine, is described as merely able to form halogen bonding because of its small polarizability. Recently, a trichloromethyl group has attracted our attention because of potential sigma effects on chlorine halogen bonding. Our studies indicated that C-Cl...O interactions may be classified as relatively strong ones, especially when enhanced by cooperative effect. The obtained results focus our attention on obtaining novel halogen bonding stabilized *crystal* structures. Our project involves utilizing various groups of potential halogen bonding acceptors in obtaining crystal structures with novel types of halogen bonds (XB), among them to *N*-oxide group as a potential XB acceptor.

The properties of the *N*-oxide group as an effective electron donor in hydrogen and halogen bonds have been the subject of many studies. Aromatic *N*-oxides have been also successfully used in synthesis of novel cocrystal structures stabilized by hydrogen bonds. Taking into consideration all these remarks we have chosen pentachloropyridine *N*-oxide as an object of our studies.

XRD studies revealed however, that in the crystal state molecules are linked by C-Cl...Cl halogen bonds and *N*-oxide groups take part in very short intermolecular *N*-oxide...*N*-oxide interactions instead of expected C-Cl...O ones. There can be indicated infinite planar ribbons of molecules linked by typical Cl...Cl contacts and forming known from literature triangle aggregates -  $X_3$  synthons in the crystal structure (see figure). These ribbons are furtherly ordered into herringbone motifs. A set of observed intermolecular interactions has been analyzed with the use of Hirshfeld surface tools.

Computations based on quantum chemistry methods (DFT- $\omega$ B97XD/6-311+G(d)) let us for a more detailed description of both kinds of intermolecular interactions. In the  $X_3$  synthon non-additive effects are relatively low and rather meaningless in the chain of molecules linked by *N*-oxide...*N*-oxide interactions indicating in the both cases very small cooperative effects.



#### References:

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**Keywords:** Halogen bonds, N-oxide group, energy of intermolecular interactions