When atoms getting close: Shortest carbon-chlorine single bond detected

May 4 2009

The description of compounds and interactions between atoms is one of the basic objectives of chemistry. Admittedly, chemical bonding models, which describe these properties very well, already exist. However, any deviation from the normal factors may lead to improving the models further. Chemists with Professor Thomas M. Klapötke at Ludwig-Maximilians-Universität (LMU) München, Germany, have now analyzed a molecule, which has an extremely short bond length.

As reported by the researchers in *Nature Chemistry*, the carbon atom and the chlorine atom in the so-called chlorotrinitromethane molecule are only 1.69 Angstroms apart from one another. "Non-covalent interactions are one of the factors responsible for this short distance", declared Göbel, whose doctoral thesis revealed the new results. "A better understanding of these interactions is important and useful in all areas, where molecular recognition and self-assembly come into play."

Chemical bond models that have been successfully used for well over a century assume that a good description of the properties of a compound can be obtained while ignoring all but the nearest-neighbour bonding interactions. The idea that electrostatic interactions between second, third and even further neighbors are important and should not be ignored has not been a common notion so far. The team of Professor Thomas M. Klapötke of the Department of Chemistry and Biochemistry at LMU Munich, primarily concerned with the synthesis and investigation of new high-energy materials, has now demonstrated for the first time that even second and third neighbors can have a decisive effect on the properties of a chemical bond.

For their investigation, the researchers chose the so-called chlorotrinitromethane molecule, a compound, consisting of the halogen chlorine and the pseudohalogen trinitromethyl group. The latter is composed of one carbon atom and three nitro groups. The trinitromethyl unit belongs to the group of pseudohalogens, which has properties similar to those of the halogens. Both groups are composed of non-metals, which are generally present in the gaseous or liquid state and form salts with metals. Contrary to the halogens, however, the pseudohalogens, instead of being true chemical elements, are chemical groups composed of different elements.

Using X-ray structural analysis, the researchers succeeded for the first time in revealing the internal structure of the chlorotrinitromethane molecule and drawing conclusions concerning the distances between the individual atoms. In their analyses, the chemists came up against a particularly interesting property of the chlorotrinitromethane molecule, namely the distance between its chlorine atom and its carbon atom is only 1.69 Angstroms. An Angstrom is 10-7 millimeters. The distance, now detected between the atoms, is the shortest distance ever observed for comparable chlorine-carbon single bonds. All previously measured distances fall within the range of approximately 1.71 and 1.91 Angstroms.

By means of theoretical calculations, carried out in cooperation with Professor Peter Politzer and Dr. Jane S. Murray of the University of New Orleans in the USA, the researchers were able to reproduce the distribution of electrical charges within the molecule. It turned out that the chlorine atom has a completely positive electrostatic potential, a rare case, since chlorine usually has a negative electrostatic potential in other molecules.

Together with the charge distributions of the remaining atoms, this finding explains why the chlorine and carbon atoms are linked so tightly to one another. The results impressively show that electrostatic interactions between atoms within a molecule can have a significant effect on bond lengths, even if these atoms are not linked directly to one of the two atoms that form the bond.

In the case of chlorotrinitromethane, this effect is particularly pronounced and leads to an unusually short chlorine-carbon bond. However, it could be of importance in various other cases, especially in areas, where molecules recognize one another and assemble to larger structures. These mechanisms play an important role, for example, in biological systems and in nanotechnology.

More information: "Chlorotrinitromethane and its exceptionally short carbon-chlorine bond"; Michael Göbel, Boris H. Tchitchanov, Jane S. Murray, Peter Politzer and Thomas M. Klapötke; *Nature Chemistry* online,3 May 2009 DOI: 10.1038/nchem.179

Source: Ludwig-Maximilians-Universität München