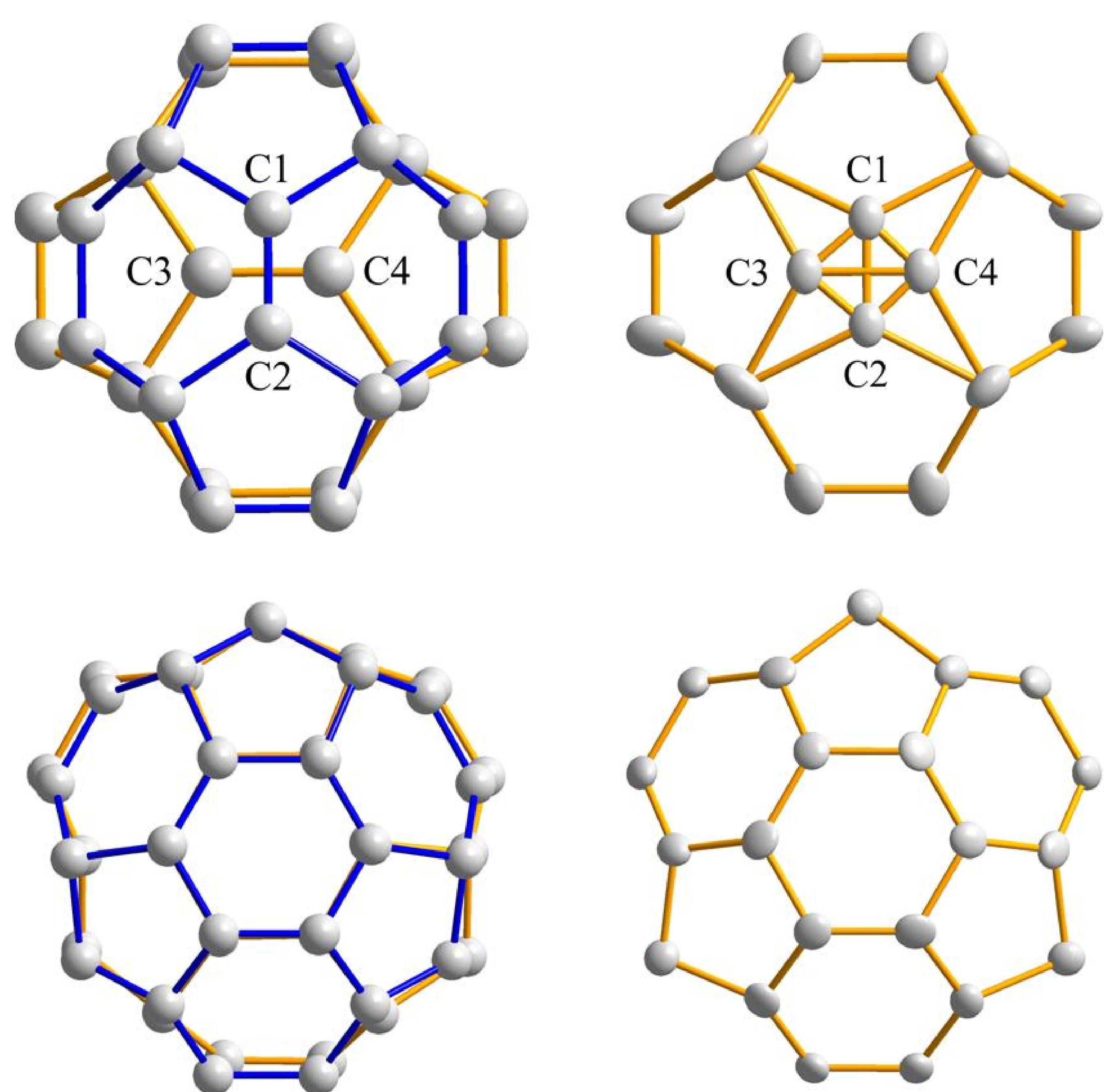




Introduction

Since higher fullerenes have been discovered, it has been shown that the existence of several structural isomers complicates drastically their investigation as well as their structural determination. Although combining some restrains (the isolated pentagon rule (IPR), the presence of twelve 5-membered and n 6-membered rings, etc.) with NMR studies has usually allowed confirming the molecular structures of fullerene species, a direct method of structure determination, such as X-ray crystallography, is envisaged to solve the query of a single-isomer recognition. The virtually spherical shape of all fullerenes as well as their mobility in the crystal lattice are responsible for the generally poor quality of the fullerene crystals. Derivatization is an efficient approach for solving this problem. In particular, halogenation has emerged as a powerful tool for obtaining well crystallized C_{60} , C_{70} and C_{76} fullerene derivatives. [1,2] Notwithstanding that halogenation partially lifts the conjugation of the π -electrons, the overall connectivities of the carbon skeleton have been found to persist.

Crystal structure of $C_{78}Cl_{18}$

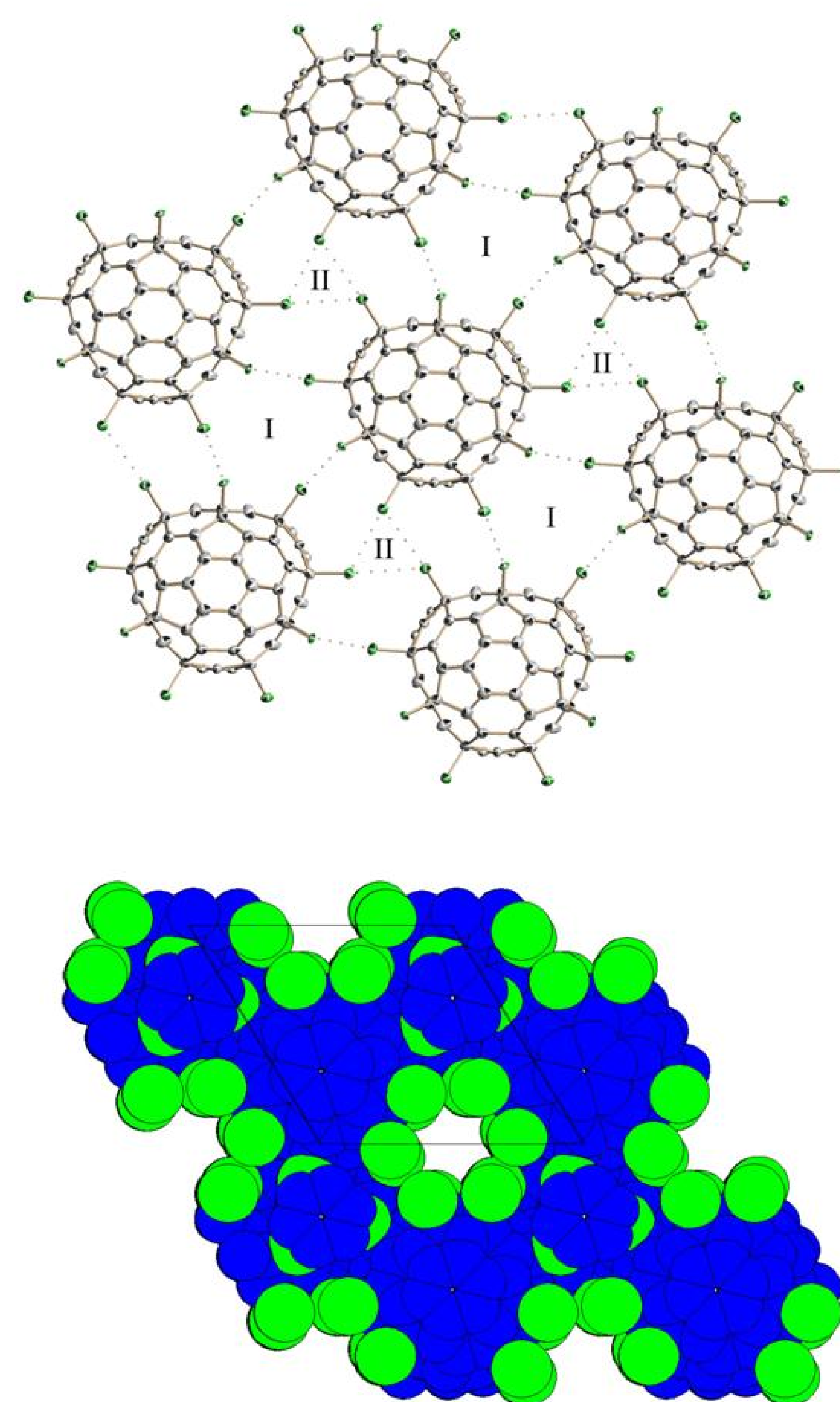


$C_{78}Cl_{18}$ molecule possesses C_{2v} symmetry. In the crystal structure the molecule is statistically disordered around the threefold axis. Since the geometry of $C_{78}Cl_{18}$ is very close to D_{3h} symmetry, the position of chlorine as well as carbon atoms, except these connected through equatorial bonds (C1-C2 and C3-C4), virtually coincide under 120° rotation. Such kind of disordering does not prevent a reliable structure determination. The relative site occupancies of mentioned bonds reveal the isomer structure. Analysis of the structure gives the ratio C1-C2 to C3-C4 of 0.65 : 0.35 which corresponds to $C_{78}C_{2v}'$ isomer (theoretically 0.66 : 0.33). The rigid body analysis showed that some deviation from D_{3h} symmetry is observed only for equatorial pyracylene fragments, the deviation for other atoms is less than the error of measurement. As it can be seen from the figures above, only the carbon atoms involved in pyracylene fragments are characterized by some prolongation of thermal ellipsoids. Thus, some bond distances including intramolecular Cl-Cl contacts can be accurately determined.

Experimental

The fullerene halide was obtained through chlorination of pure, isolated C_{2v}' C_{78} (0.1 mg) in 1 ml mixture of Br_2 : $TiCl_4$ (1 : 100 v/v) in a closed glass ampoule. [2] Yellow crystals formed directly on the glass wall after heating the mixture at 100° C for a few days. The product was found to be stable on air for at least one month. X-ray diffraction data were obtained using a Bruker APEX II CCD diffractometer ($Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite monochromator). The crystal structure was solved and all atoms were refined in the anisotropic approximation using SHELXTL.

Tunnels in $C_{78}Cl_{18}$



Within the crystal packing of $C_{78}Cl_{18}$, the chlorine atoms form a 3-D Cl**Cl network with short intramolecular Cl**Cl distances. Such an orientation in the crystal leads to formation of 2 different "empty spaces" (I, II). The first of them extends along [001] of the hexagonal lattice, thus forming tunnel-like voids. The inner "surface" of these tunnels is formed only by chlorine atoms. The green circles on the bottom picture represent the van-der-Waals radii of chlorine atoms. The "empty" space is clearly visible in the center. The diameter of the tunnels is approximately 2.4 Å, big enough to accommodate small molecules as hydrogen for example.

Conclusion

The first crystal structure of a chlorinated single isomer of C_{78} fullerene is presented. The crystallographic analysis confirms the proposed in the literature symmetry of the cage. The formation of 3-D tunnels along [001] provides interesting field for future study of the nature of this phenomenon and its usage.

References

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- [2] K. Simeonov, K. Yu. Amsharov, M. Jansen, *Angew. Chem.* **2007**, in press.