

The Role of Inter- and Intramolecular H...H Contacts in the Crystals of Carboranes

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On the basis of the high-resolution X-ray diffraction study of the electron density distribution function as well as quantum-chemical calculations of the crystal structures the attractive intramolecular contacts in the crystals of both aryl-substituted carboranes and metallacarboranes have been investigated. Their energy values have allowed creating the scheme, for the estimation of the lattice energy using only the X-ray diffraction data for the carborane derivatives.

Using R. Bader's theory "Atoms in Molecules" for both X-ray data and relaxed quantum-chemical scans of the potential energy surfaces of aryl-substituted carboranes along the coordinate defining the conformation of the substituent, it was found that despite the presence of close intramolecular H...H contacts between the hydrogen atoms of an aryl ring and those of the carborane moiety, all studied mono-substituted aryl-carboranes are characterized by the absence of a barrier to the rotation of the ring, due to the presence of the attractive interaction between the corresponding pairs of hydrogen atoms. Upon such barrierless rotation of the aryl rings the changes of the C-C and C-B bonds lengths of the carborane icosahedrons occur due to the transfer of the π -density of an aromatic ring to the corresponding antibonding orbital of one of these bonds. Close examination of the C-C bond properties in *o*-carboranes has allowed to suppose, that this bond can be described as a "single π -bond".

Keywords: inter- and intramolecular interactions, electron density distribution in bonds, topological properties of charge distribution