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New concepts of the structures of 11-vertex carba-*closo*-boranes based on the data of vibrational spectroscopy and quantum-chemical calculations

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We pioneered to obtain the vibrational (Raman and IR) spectra of 11-vertex carba-*closo*-boranes: the monocarbaborane anion $[2\text{-}CB_{10}H_{11}]^-$ (**1**) as its tetramethylammonium and cesium salts and the neutral dicarbaborane molecule $2,3\text{-}C_2B_9H_{11}$ (**2**) (Fig. 1). Quantum-chemical calculations of the geometry and vibrational mode frequencies and eigenvectors were performed in the framework of the density functional theory (DFT). Based on the optimized geometry, we carried out the topological analysis according to Bader[1] for the electron density distribution (EDD) function in molecules **1** and **2**.

The presence of two low-frequency (180—250 cm^{-1}) modes in the Raman and IR spectra of compounds **1** and **2** indicates unambiguously that both polyhedra are "non-rigid" (*i.e.*, they are easily deformable). This fact sharply distinguishes these structures from the previously studied[2] 12-, 10-, 6-, and 5-vertex *closo*-polyhedra, which spectra contain no normal modes with frequencies lower than 450 cm^{-1}. Both the experimental[3—5] and calculated interatomic distances between the hexacoordinated B(1) atom and pentacoordinated B atoms in clusters **1** and **2** are unusually long (2.05—2.08 Å). This agrees with the results of topological analysis of the EDD, according to which the corresponding two-center B—B bonds (shown in Fig. 1 by dashed lines) are absent (because critical points of the (3, −1) type between these atoms are absent). This produces two pentagonal faces with a substantially decreased electron density compared to the rest part of the polyhedra. The calculation of vibrational mode frequencies and eigenvectors shows that one of the low-frequency modes is a bending mode with the predominant involvement of the B(4), B(5), B(6), and B(7) atoms, while the second low-frequency mode represents mainly a vibration with a large amplitude of the B(1) atom in the C(2)B(1)B(3) "handle" of molecule **1** or in C(2)B(1)C(3) of molecule **2** with respect to the mirror plane. Evidently, both deformations are eased by the absence of the aforementioned B—B bonds. Thus, monocarbaborane **1** and dicarbaborane **2** are not deltahedra and do not possess *closo*-structure, which is traditionally ascribed to them due to their $2n + 2$ bonding skeletal electrons.[6] It should be noted that the specific properties of the 11-vertex polyhedra have been observed previously,[3,6—8] due to which they were attributed to "disobedient skeletons"[9] known because of their "fragility."[10]

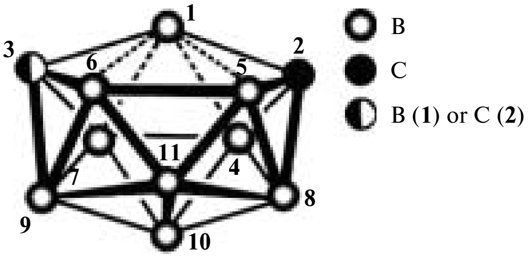

Fig. 1. 11-Vertex polyhedra **1** and **2** with atom numbering. The absent bonds are designated by dashed lines.

Experimental

Substances **1** and **2** were synthesized according to described procedures.[11,12] Raman spectra of solid compounds were recorded on T64000 and U-1000 laser Raman spectrometers (Jobin Yvon) using excitation with a line of 514.5 nm from an SP-2020 Ar^+ laser. IR spectra were obtained on an M-82 spectrophotometer (Carl Zeiss) and a Nicolet Magna-750 FTIR spectrometer for KBr pellets and Nujol and hexachlorobutadiene mulls.

The geometry optimization and calculation of vibrational mode frequencies and eigenvectors for isolated anion **1** and molecule **2** were carried out by the DFT method (B3LYP functional) in the 6-311++G(d,p) basis set using the G94W program package.[13] The topological analysis of the EDD function according to Bader[1,14] was based on the results of calculations.

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