**Abstract**

Using density functional theory (DFT) methods, we shed light on the structural, optical, electronic and nonlinear optical (NLO) properties of three derivatives of 9,12-diiodo-1,2-dicarba-closo-dodecaborane (12) (C2H10B10I2). The DFT and TD-DFT methods are considered very precise and practical to optimize the ground and excited state geometries, respectively. A vibrant intra-molecular charge transfer from highest occupied molecular orbitals (HOMOs) to the lowest unoccupied molecular orbitals (LUMOs) was observed in all compounds. The geometrical parameters of experimental crystal structure, i.e., bond lengths/angles have been successfully reproduced. The HOMO and LUMO energies, as well as their energy gaps (Eg) were also calculated and compared with each other for all derivatives. The effect of attached groups on electronic, optical and NLO properties along with detailed structure-property relationship was discussed. For nonlinear optical (NLO) response, the CAM-B3LYP functional along with relatively larger basis set 6-31+G\*\* (for hydrogen, carbon, boron and oxygen atoms) and LANL2DZ (for Iodine atoms) have been used to optimize the compounds at ground states. The calculation of second-order NLO polarizabilities (*β*tot) shows that compounds **2** and **3** possess the *β*tot amplitudes of 3029 and 4069 a. u., respectively, with CAM-B3LYP method which are reasonably larger than similar prototype molecules. Owing to their unique V-shapes, the nonlinear anisotropy values are found to be 0.63, 0.34 and 0.44 for compounds **1-3**, respectively, which show the significant two-dimensional character of these compounds. Thus, the NLO amplitudes as well as nonlinear anisotropies indicate that the above-entitled compounds are good contenders for optical and NLO applications.