A Computational Study on Molecular Structure and Spectral Properties of Halogenated Sumanene

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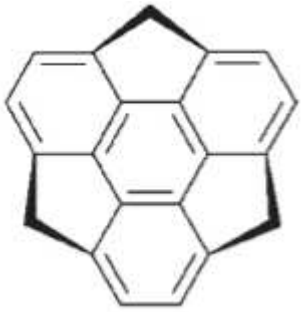
Bowl-shaped π-conjugated compounds have been attracting great interests because of their promising potential for electrical materials [1]. They are a group of key materials in the science of nonplanar π-conjugated carbon systems. Sumanene ($C_{21}H_{12}$) is a C_{3v} symmetric structure of fullerenes and a bowl-shaped π-conjugated aromatic compound with possessing interesting structural and physical properties, and it has been synthesized successfully by Sakurai, Daiko and Hirao [2]. Although there have been many experimental and theoretical studies on sumanene [3], the halogenated sumanenes have not been investigated computationally up to now. The use of DFT methods optimized geometries approximately reproduces the experimental values for the bowl-to-bowl inversion barrier of sumanene and its derivatives [4].



Benchmark studies usually analyze the difference between DFT and experiment statistically. The linear regression is performed by means of a least-squares fit, from which we obtain the slope as well as the scatter with respect to the regression line (SPSS program) to examine the performance of different implementations and functionals for the title compound at first. A computational study was conducted on fluorinated, chlorinated, and brominated sumanenes, which were subjected to the analysis of changes of the molecular electrostatic potential surfaces, spectral properties (Vibrational and NMR spectra) and bowl-to-bowl inversion barrier properties. The bowl shaped geometry and other properties were significantly affected by the substitution of halogens.

All calculations within DFT were performed using Gaussian 09 [5]. DFT calculations were performed by means of the hybrid, non-local exchange and correlation functional of Becke-Lee, Parr and Yang (B3LYP) [6] and [7].

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