

Structure and NMR and UV Spectra of Strained Cyclophanes with Small Bridges

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Abstract

The objectives of this PhD dissertation were (a) analysing the structures of different kinds of cyclophanes using density functional theory (DFT) and comparing with available experimental results, aiming for the understanding of the structural phenomena as well as determining the missing structural parameters for the known and hypothetical molecules, (b) carrying out DFT calculations of the NMR spectral parameters and comparing them with the literature and measured experimental results, and (c) calculating the absorption and emission wavelengths of the $[m.n]$ paracyclophanes, with $m, n = 2 - 4$. It should be stressed that the calculations have been preceded by the measurement of NMR spectra and UV/Vis and emission spectra performed in the Institute of Organic Chemistry and Institute of Physical Chemistry, respectively. To achieve these objectives, the molecules considered were divided in to three sets.

The studies conducted on the first set of molecules, [2.2]paracyclophane and its derivatives, show that the B3LYP functional is not well suited for the geometry optimization of the paracyclophanes studied. The calculated NMR parameters were compared with the experimental values. The results of the calculations involving only protons were compared with very accurate chemical shifts and $^2J_{HH}$ and $^3J_{HH}$ coupling constants determined in IChO PAN and IChF PAN. The theoretical vicinal J_{HH} coupling constants in the aliphatic bridges using 6-311G(d,p), cc-pVTZ, or Huz-IV basis sets reproduce the experimental values with an approximate rms error of about 1.3 Hz, regardless of the basis set used.

The optimized geometries of the second set of molecules, cyclophanes with ethylene bridges (cyclophenes), showed that only ω B97X-D/6-311++G(2d,2p) and ω B97X-D/cc-pVQZ yielded values of the $C_{sp^3}C_{sp^3}$ bond lengths close to the experimental data. ω B97X-D provides better results for bond lengths but the $C_{sp^2}C_{sp^3}C_{sp^3}C_{sp^2}$ torsional angles are not satisfactorily reproduced. Contrary to the calculations of geometries, an agreement between the values of the NMR parameters obtained using ω B97X-D/cc-pVQZ and the experimental ones is the poorest. Taking into account that most of the results of the different calculations show the same

qualitative trends, the structural and NMR properties of the hypothetical cyclophanes are assumed to be correctly represented by the calculated values.

For the third set of molecules $[m.n]$ paracyclophanes, $m, n = 2 - 4$, the DFT calculations satisfactorily reproduced the experimental chemical shifts, coupling constants, and absorption and emission wavelengths. Inclusion of dispersion and long-range corrections to the functionals improves the geometry optimizations, except for the $C_{sp^2}C_{sp^3}C_{sp^3}C_{sp^2}$ torsional angle of $[2.2]$ paracyclophane. Also in this case, the results of the calculations of involving only protons were compared with very accurate chemical shifts and $^2J_{HH}$ and $^3J_{HH}$ coupling constants values determined in IChO PAN and IChF PAN.