Semi-Experimental Equilibrium Structure Determinations by Employing B3LYP/SNSD Anharmonic Force Fields: Validation and Application to Semirigid Organic Molecules

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Rok wydania

2015

Czasopismo

Journal of Physical Chemistry A

Numer woluminu

119

Strony

2058-2082

DOI

10.1021/jp511432m

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

This work aims at extending the semi-experimental (SE) approach for deriving accurate equilibrium structures to large molecular systems of organic and biological interest. SE equilibrium structures are derived by a least-squares fit of the structural parameters to the experimental ground-state rotational constants of several isotopic species corrected by vibrational contributions computed by quantum mechanical (QM) methods. A systematic benchmark study on 21 small molecules (CCse set) is carried out to evaluate the performance of hybrid density functionals (in particular B3LYP) in the derivation of vibrational corrections to rotational constants. The resulting SE equilibrium structures show a very good agreement with the corresponding geometries obtained employing post-Hartree−Fock vibrational corrections. The use of B3LYP in conjunction with the double-ζSNSD basis set strongly reduces the computational costs, thus allowing for the evaluation of accurate SE equilibrium structures for medium-sized molecular systems. On these grounds, an additional set of 26 SE equilibrium structures including the most common organic moieties has been set up by collecting the most accurate geometries available in the literature together with new determinations from the present work. The overall set of 47 SE equilibrium structures determined using B3LYP/SNSD vibrational corrections (B3se set) provides a high quality benchmark for validating the structural predictions of other experimental and/or computational approaches. Finally, we present a new strategy (referred to as the template approach) to deal with the cases for which it is not possible to fit all geometrical parameters due to the lack of experimental data.

Słowa kluczowe

Chemical structure, Equilibrium, Mathematical methods, Molecular structure, Molecules