

Hydrogen bonding as a modulator of aromaticity and electronic structure of selected *ortho*-hydroxybenzaldehyde derivatives.

Autorzy

Aneta Jezierska-Mazzarello

Jarosław J. Panek

Halina Szatyłowicz

Tadeusz M. Krygowski

Rok wydania

2012

Czasopismo

Journal of Physical Chemistry

A

Numer woluminu

116

Strony

460-475

DOI

10.1021/jp205730t

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

Properties of hydrogen bonds can induce changes in geometric or electronic structure parameters in the vicinity of the bridge. Here, we focused primarily on the influence of intramolecular H-bonding on the molecular properties in selected *ortho*-hydroxybenzaldehydes, with additional restricted insight into substituent effects. Static models were obtained in the framework of density functional theory at B3LYP/6-311+G(d,p) level. The electronic structure parameters evolution was analyzed on the basis of Atoms In Molecules (AIM) and Natural Bond Orbitals methods. The aromaticity changes related to the variable proton position and presence of substituents were studied using Harmonic Oscillator Model of Aromaticity (HOMA), Nucleus-Independent Chemical Shift (NICS) and AIM-based parameter of Matta and Hernández-Trujillo. Finally, Car-Parrinello molecular dynamics was applied to study variability of the hydrogen bridge dynamics. The interplay between effects of the substitution and variable position of the bridged proton was discussed. It was found that the hydrogen bond energies are ca. 9-10 kcal/mol, and the bridged proton exhibits some degree of penetration into the acceptor region. The covalent character of the studied hydrogen bond was most observable when the bridged proton reached the middle position between the donor and acceptor regions. The aromaticity indexes showed that the aromaticity of the central phenyl ring is strongly dependent on the bridged proton position. Correlations between these parameters were found and discussed. In the applied time-scale, the analysis of time evolution of geometric parameters showed that the resonance strengthening does not play a crucial role in the studied compounds.

Adres publiczny

<http://dx.doi.org/10.1021/jp205730t>

<https://www.acs.org/content/acs/en.html>

Plik został wygenerowany dnia 2026-08-25 05:43:31

Adres w repozytorium <https://old.chem.uni.wroc.pl/pl/repozytorium/8b3z0sX>.