Tautomerism of sterically hindered Schiff bases. Deuterium isotope effects on ^{13}C chemical shifts.

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2005

Czasopismo

Journal of Physical Chemistry A

Numer woluminu

109

Strony

4464-4473

DOI

10.1021/jp0445977

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

A series of sterically hindered *o*-hydroxy Schiff bases derived from *o*-hydroxyaceto- and benzophenones with very short intramolecular hydrogen bonds were described qualitative and quantitatively by deuterium isotope effects on ^{13}C chemical shift, $^{n}\Delta C(XD)$, $^{n}\Delta F(XD)$, $^{1}J(N,H)$ coupling constants, δNCH_3 chemical shifts and UV spectra. All the investigated compounds are found to be tautomeric. The tautomeric character is described by the signs of the deuterium isotope effects on the ^{13}C chemical shifts. For the 3-nitro-5-chloro derivatives at low temperature, the equilibrium is shifted almost fully toward the proton transferred form in CD_2Cl_2. Intrinsic deuterium isotope effects on chemical shifts of these compounds as well as $^{1}J(N,H)$ coupling constants suggest that a zwitterionic resonance form is dominant for the proton transferred form. Structures, ^{1}H , ^{19}F, and ^{13}C chemical shifts, and deuterium isotope effects on ^{13}C chemical shifts are calculated by ab initio methods. The potential energy functions and the total deuterium isotope effects are calculated, and they are shown to correspond well with the experimental findings.

Słowa kluczowe

Equilibrium, Hydrogen isotopes, Isotope effects, Reaction mechanisms, Solvents

Adres publiczny

https://doi.org/10.1021/jp0445977

Strona internetowa wydawcy

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