Secondary isotope effects on ^{13}C and ^{15}N chemical shifts of Schiff bases revisited.

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Rok wydania

2013

Czasopismo

Zeitschrift für Physikalische Chemie - International Journal of Research in Physical Chemistry and Chemical Physics

Numer woluminu

227

Strony

917-927

DOI

10.1524/zpch.2013.0378

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

An analysis is presented of secondary deuterium isotope effects on ^{15}N and ^{13}C chemical shifts of the methylamine Schiff base of 4,6-dimethoxysalicylaldehyde. It is shown that for this compound existing as an equilibrium between an OH and a NH-form, the secondary isotope effects depend on the OH/NH ratio giving a function with a maximum and a minimum.

Secondary deuterium isotope effects on ^{13}C and ^{15}N chemical shifts are compared in a broader range of compounds and the above trend is confirmed. Changes in the dielectric constants of the medium with temperature are found to be rather unimportant for the change in equilibrium. Equilibrium isotope effects on chemical shifts are shown to be important. The magnitudes of the isotope effects are correlated both to intrinsic and equilibrium isotope effects. The latter correlate to the shape of the two-potential well, the energy difference and the difference in chemical shifts of the two tautomers.

Słowa kluczowe

Secondary Deuterium Isotope Effects, Chemical Shifts, Schiff bases, DFT calculation, intramolecular hydrogen-bonding

Adres publiczny

http://dx.doi.org/10.1524/zpch.2013.0378