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NICS values in gas phase, implicit solvents and micro-solvated systems

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ABSTRACT

Effect of explicit micro-solvation on the nucleus-independent chemical shift (NICS) values of cyanuric acid (CA) and hydroquinone (HQ) were studied. It was shown that the decrease in the NICS values of the micro-solvated CA and HQ can be interpreted basis on the strength of the hydrogen bonds formed between the solvating molecules (H_2O, CH_3OH, NH_3) and the aromatic compounds. Also, the NICS values for 8 molecules in 10 different solvents were calculated and an equation as $\mathrm{NICS}(\varepsilon) = \mathrm{NICS}_{aq} - \alpha\varepsilon^{\beta}$ was proposed, where, NICS_{aq} is the NICS value in water, ε is the dielectric constant of the solvent and α and β are constants. It was found that both implicit solvents and micro-solvation decrease the absolute values of NICS index. However, effect of micro-solvation on the NICS values was more than the effect of implicit solvents.

1. Introduction

There are several criteria for evaluation of aromaticity or cyclic π-electron delocalization. These criteria investigate the chemical compounds from structure, reactivity, energy, and magnetic properties points of view [1]. The harmonic oscillator model of aromaticity (HOMA) is used for determination of aromaticity basis on geometrical parameters of the molecule [2–4]. The HOMA method is based on the tendency of aromatic rings toward planarity and bond length equalization [2–4]. Since the aromatic molecules are more stable than their reference models, the aromatic stabilization energy (ASE) is used as an index for aromaticity [5–7]. Furthermore, the stability of aromatic compounds results in low reactivity, however, the reactivity is not a general criterion and has many exceptions [1,8].

Magnetic criteria, such as proton chemical shift, magnetic susceptibility and nucleus-independent chemical shift (NICS), are the most frequently used indices for determination of aromaticity [1]. In the NICS method, in order to probe aromaticity the chemical shielding of a virtual molecule (Bq) is computed [9–11]. The NICS index has been applied for polycyclic compounds [12,13], aromatic molecules containing heterogeneous atoms [14,15] and metallic compounds [16,17].

Usually the NICS index is calculated for isolated molecules while these molecule can be micro-solvated in the presence of protic solvents. Junqueira and Santos [18] studied the solvent effect on the aromaticity of benzene using the NICS index. They founds that solvent changes the aromaticity so that benzene in condensate phase with explicit molecules is slightly more aromatic than isolated benzene [18].

In this work, effect of micro-solvation with H_2O, CH_3OH and NH_3 molecules on the aromaticity of cyanuric acid (CA) and hydroquinone (HQ) is studied. Also, the solvent effect on the aromaticity of CA and HQ is investigated using polarizable continuum model (PCM).

2. Computational details

The structures of all isolated and micro-solvated molecules were fully optimized employing B3LYP functional using 6-311++G(d,p) basis set. To obtain the thermodynamic data, enthalpies and Gibbs energies of micro-solvation, the frequency calculations were carried out at the same level of theory. The solvents were modeled using Tomasi's polarized continuum model (PCM) [19]. The NICS indices were calculated at the center of the molecule ring, from the ring surface to 2 Å above the ring. The NICS calculations were performed using guage-independent atomic orbital (GIAO) method and the Bq atom as a probe. The negative values of isotropic NICS ($\mathrm{NICS_{ISO}}$) and its out-of-plane component ($\mathrm{NICS_{ZZ}}$) were reported as the aromaticity indices [10]. The calculations were carried out using Gaussian 09 software [20].

3. Results and discussion

3.1. NICS index of micro-solvated molecules

To explore effect of micro-solvation on the aromaticity, two aromatic molecules, cyanuric acid (CA) and hydroquinone (HQ),

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containing hydrogen bond donor and acceptor sites were considered. Fig. 1 shows the optimized structures of CA and HQ micro-solvated with H_2O, NH_3, and CH_3OH molecules. CA has three hydrogen bond donor and three hydrogen bond acceptor sites. Therefore, each solvating molecule forms two hydrogen bonds with the CA (dotted lines in Fig. 1). On the other hand, HQ has only hydrogen donor sites and one hydrogen bond is formed per a solvating molecule. The hydrogen bond lengths are shown in angstrom.

Fig. 2 shows effect of micro-solvation on the $NICS_{ISO}$ values of (a) CA and (b) HQ at different distances from the surface of the aromatic rings. The plots of the $NICS_{ZZ}$ values have been shown in Fig. S1 (Supplementary Materials). The NICS values calculated in the ring centers are not good indices of aromaticity, because they contain shielding and deshielding contributions of σ-framework and core electrons [21]. Therefore, we used the scan NICS values obtained at different distances above the molecule surfaces to minimize the effect of σ-framework and local circulations and ensure the main contribution to the NICS is due to π-electronic current. The $NICS_{ISO}$ values exhibit diatropic shift at short distances above the rings (0.0–0.75 and 0.0–0.6 Å for CA and HQ, respectively). The $NICS_{ZZ}$-scan curves of aromatic compounds show diatropic chemical shift with a deep minimum (large magnitude) and nonaromatic compounds show a shallow minimum with small magnitude of $NICS_{ZZ}$ [10]. Therefore, HQ with minimum $NICS_{ZZ}$ value of -25 ppm is more aromatic than CA with minimum $NICS_{ZZ}$ value of -15 ppm (Fig. S1).

Micro-solvation shifts the NICS indices of both molecules toward more positive values. In other words, micro-solvation decrease the aromaticity of CA and HQ. Furthermore, effect of NH_3 is more than that for CH_3OH and H_2O. The decrease in the aromaticity may be due to formation of hydrogen bonds between the aromatic molecules and the protic molecules (H_2O, CH_3OH and NH_3). The calculated enthalpies (ΔH) and Gibbs energies (ΔG) of the micro-solvation of CA and HQ are tabulated in Table 1. The ΔH values indicate the strength of the hydrogen bonds. The enthalpies of micro-solvation of CA with the solvating molecule is as $NH_3 > CH_3OH > H_2O$ and for HQ is $NH_3 > CH_3OH \geqslant H_2O$. The observed trends for the NICS values are in good accordance with the enthalpies of micro-solvation. Also, the enthalpies of micro-solvation of CA are larger than those for HQ, therefore, the relative decrease in the NICS values is more in the micro-solvated CA. Fig. 2 c and d shows the variations the $NICS_{ISO}$ values of micro-solvated CA and HQ versus those for the corresponding isolated molecules, respectively. Fig. S1c and d (Supplementary Materials) shows this relationship for the $NICS_{ZZ}$ values. The variation of the NICS values of the micro-solvated molecules versus those of the isolated molecules is not linear. This nonlinearity may be due to the change in the electronic structure and geometric parameters of the molecules after micro-solvation [22–24]. Furthermore, the nonlinearity for the molecules with NH_3 as solvating molecule is more. As mentioned, the hydrogen bonds between NH_3 and CA and HQ are stronger than those formed between CH_3OH and H_2O as solvating molecules and CA and HQ compounds. In addition, the deviation for the micro-solvated CA is more than that for the micro-solvated HQ. Table 1 shows that interaction energies between solvating molecules and CA are larger than those for the HQ. Therefore, as the interaction between solvating molecules and aromatic compounds increases the change in the electronic structure and aromaticity increases.

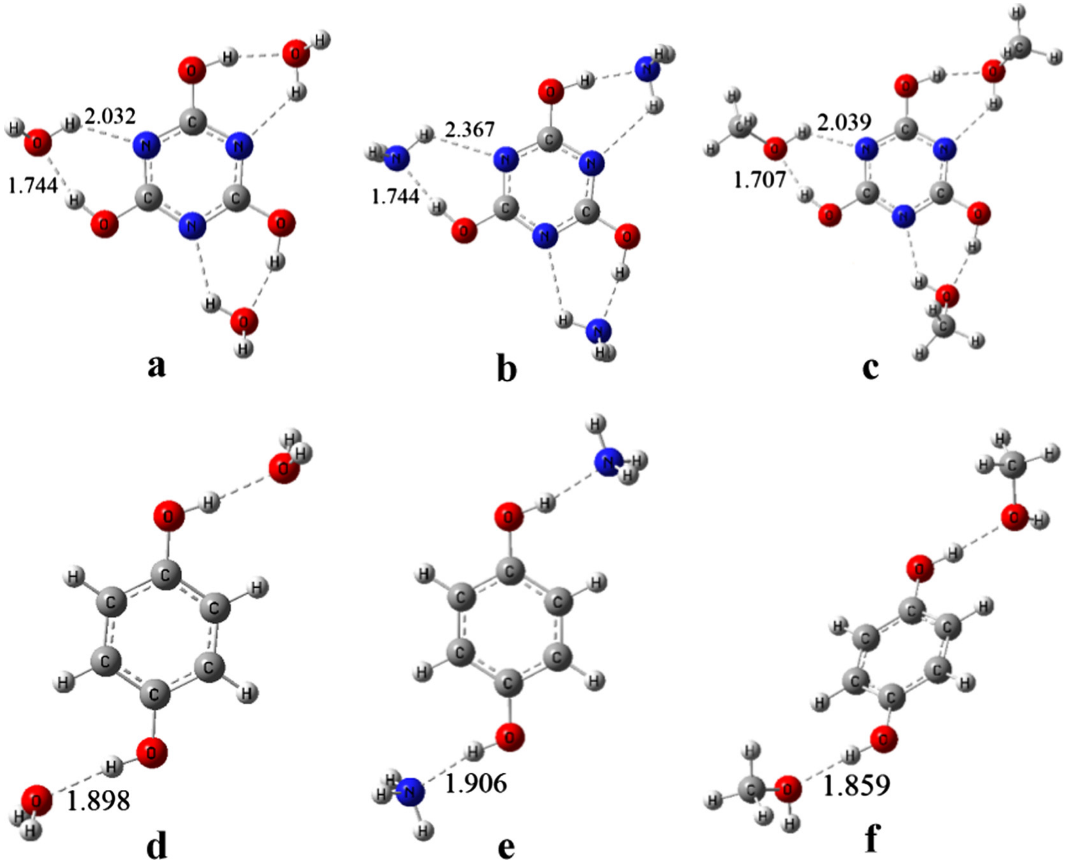

Fig. 1. Structures of (a) CA + $3H_2O$, (b) CA + $3NH_3$, (c) CA + $3CH_3OH$, (d) HQ + $2H_2O$, (e) HQ + $2NH_3$, and (f) HQ + $2CH_3OH$ optimized by B3LYP/6-311 + + G(d,p) method.