



Research paper

Design of the strongest organic Brønsted acids in gas phase



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ABSTRACT

A new type of organic Brønsted acids is proposed exhibiting very high acidity in gas phase. The calculated gas phase enthalpies (ΔH_{acid}) of deprotonation were 220–240 kcal/mol for the proposed acids with -CN substituents indicating that they can rival the inorganic carborane acid derivatives in gas phase. The hyperacidity of these compounds rises from the extra stability of the corresponding conjugate bases due to formation of a hydrogen bonding network and an aromatic five-membered ring.

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1. Introduction

Superacids are very important compounds in chemistry, therefore, considerable efforts have been made to design, synthesis and examine molecules with super- and hyperacidity [1–9]. Tian et al. [8] designed and assessed a new class of organic Brønsted acids so called single-centered hydrogen-bonded enhanced acidity (SHEA) acids. The acidity of the SHEA acids is due to strong hydrogen bonding interactions in the conjugated bases [8,10]. The reported gas phase enthalpies of deprotonation (ΔH_{acid}) for the SHEA acids with -F substituents are 260–290 kcal/mol [8]. Cyclopentadiene, C_5H_6 , forms a stable aromatic anion, $C_5H_5^-$, after deprotonation, therefore, it has been used in the design of compounds with high acidity [11–14]. The ΔH_{acid} values for C_5H_6 and $C_5(CN)_5H$ are 353.5 and 274.5 kcal/mol [11], respectively, indicating that the electron withdrawing groups, CN, increase the acidity. Also, fulvene derivatives exhibit superacidity because they form a stable aromatic ring due to bond rearrangement and electron delocalization after deprotonation [15–17]. The reported ΔH_{acid} values for the strongest acids of fulvene derivatives with CN substituents are about 240–250 kcal/mol [15–17]. The derivatives of carborane acid ($CB_{11}H_{12}H$) and dodecaborane acid ($B_{12}H_{12}H_2$) are known as the strongest inorganic acids [18–23]. The acidity of the carborane acids is due to excellent charge delocalization ability of their cage-shape boron structure. Also, addition of electron withdrawing groups is another strategy to enhance their acidity. For example, the reported ΔH_{acid} value of carborane acid with F substituents, $CB_{11}F_{12}H$, is 215.0 kcal/mol [18]. Therefore, there is no organic acid

with acidity higher than or comparable with the carborane acid derivatives with electron withdrawing substituents.

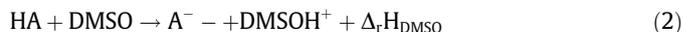
In this work, we used three strategies including aromaticity, hydrogen bond interaction and substituting electron withdrawing groups, to reach stable conjugate bases and design superacid compounds.

2. Computational details

The structures of the proposed acids and their conjugate bases were optimized using B3LYP method and 6-311++G(d,p) basis set. The enthalpy (ΔH_{acid}) and Gibbs free energy (ΔG_{acid}) of deprotonation in gas phase, reaction (1), were used to compare the acidity of the compounds.



The ΔH_{acid} and ΔG_{acid} values were corrected for the zero point energy (ZPE). The calculations in DMSO solvent were performed by Tomasi's polarized continuum model (PCM) [24]. The Gaussian 09 software was used for the calculations [25]. The enthalpies of protonation of DMSO by the proposed acids in solution ($\Delta_r H_{\text{DMSO}}$) were calculated according to reaction (2):



The pK_a s of the acids in DMSO solvent were estimated using the $\Delta_r H_{\text{DMSO}}$ values and the following empirical equation [13]

$$pK_a(\text{theor}) = 0.661 \times \Delta_r H_{\text{DMSO}} - 7.7 \quad (3)$$

The accuracy of Eq. (3) has been confirmed for a wide variety of neutral organic acids with the average absolute error of 1.1 in pK_a unit [13]. The Nucleus-Independent Chemical Shift (NICS) method

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was used for evaluation of the aromaticities of the compounds [26]. The NMR shielding tensors were computed with the Gauge-Independent Atomic Orbital (GIAO) method [27] at the center of the five-membered ring, NICS(0), and 1 Å above it, NICS(1), using a Bq atom as a probe [28,29]. The negative values of isotropic (NICS_{ISO}) and out-of-plane components (NICS_{ZZ}) of the shielding tensor were used to compare the aromaticities of the acids and their conjugate bases. The NMR chemical shift tensors were also calculated using B3LYP/6-311++G(d,p) method.

3. Results and discussion

Fig. 1 shows the structures of the proposed acids. The optimized structures of the acids as well as their geometrical parameters (bond lengths, angles and dihedrals) have been collected as [Supplementary Materials \(Fig. S1\)](#). The acids are planar (point group=C_s) poly enol compounds with a cyclopentadiene ring. Two isomers were considered for each structure, odd (I, III, ...) and even (II, IV, ...) numbers in Fig. 1. The isomers labeled by odd numbers (I, III, V, ...) are more stable than the corresponding isomers labeled with even numbers (II, IV, VI, ...). Also, the keto tautomers are the other possible isomers for the structures shown in Fig. 1. The calculations showed that for the structures with strong electron withdrawing substituents (CN), the enol forms (V, VI, XI, XII, XVII, XVIII) are more stable than the corresponding keto forms. For the structures without any electron withdrawing groups, the

keto forms are more stable. Fluorine increases the stability of the enol isomers, however, the keto forms with F substituents are about a few kcal/mol more stable.

Since the acids in Fig. 1 have different acidic hydrogen atoms, it is expected to have different conjugate bases for each acid. However, some of the conjugate bases are not stable so that they converted into the more stable isomers during structure optimization. Fig. 2 shows the structures of the stable conjugate bases, where, the letters **a**, **b** and **c** indicate the different conjugate bases of the same acid and the numbers are relative energies in kcal/mol. The optimized structures of the conjugate bases as well as their geometrical parameters (bond lengths, angles and dihedrals) have been collected as [Supplementary Materials \(Fig. S2\)](#). After deprotonation, bond rearrangements result in formation a five-membered aromatic ring. Also, formation of a stronger hydrogen bonding network stabilizes the conjugate bases. Furthermore, substituting the electron withdrawing groups, F and CN, increased the stability of the conjugated bases and consequently, enhanced the acidity. It should be mentioned that the hydrogen bond interactions present in both acids and their conjugate bases, however, the hydrogen bonding interactions in the bases are stronger [8,10,17]. Fig. 3 compares the hydrogen bond distances and partial atomic charges in the acid I and its conjugate base. The distance of OH...OH hydrogen bond in the acid I is 1.88 Å. After deprotonation, the hydrogen bond is formed between the hydrogen of OH group and oxygen of the carbonyl group, OH...O=C, with shorter H...O

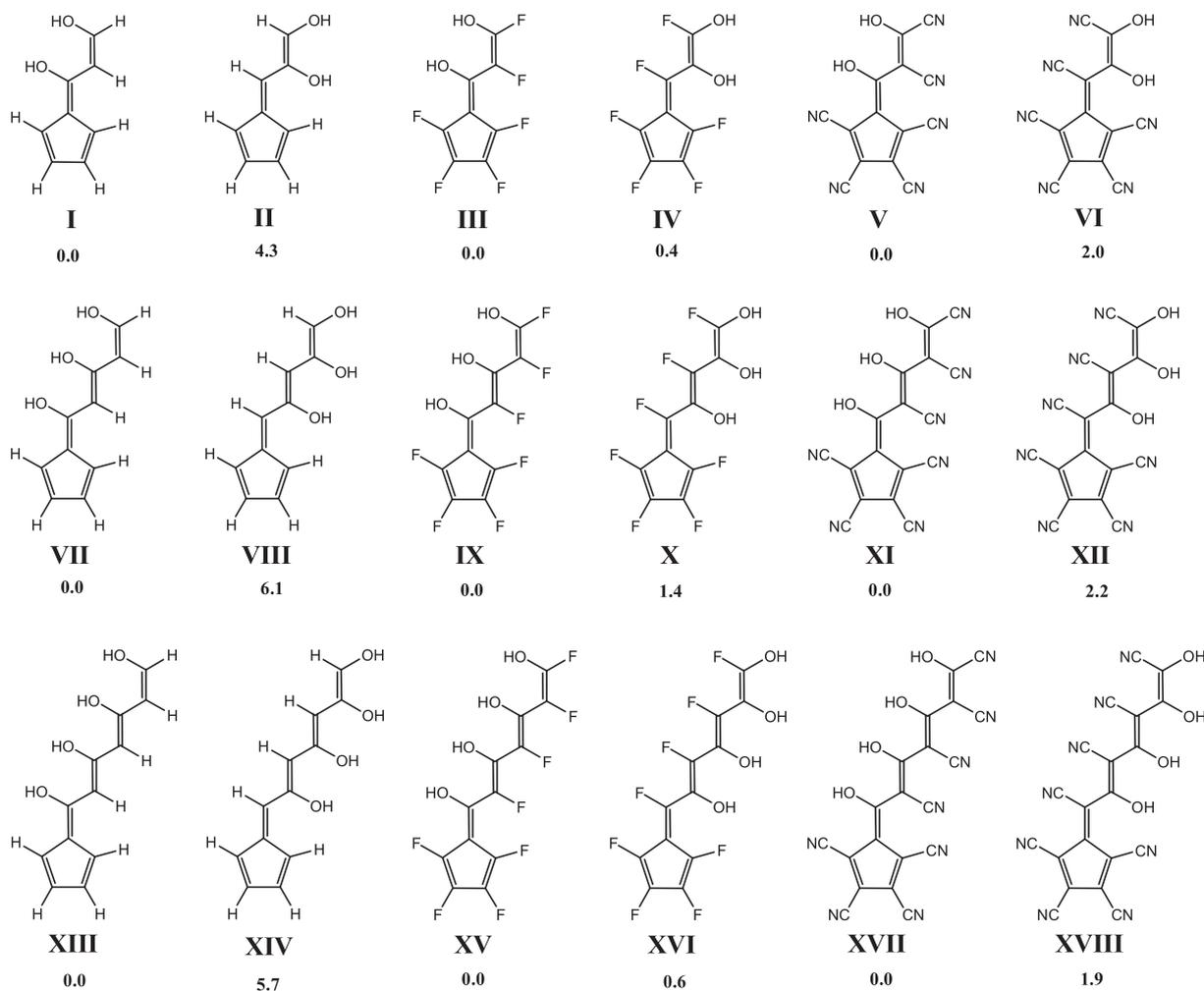


Fig. 1. Schematic representation of the proposed superacids. The numbers are relative energies of the isomers in kcal/mol.

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