



# Comprehensive DFT calculations on organic sulfuric acid derivatives to design of powerful neutral organic superacids

Hamid Saeidian<sup>1</sup> · Bahareh Shams<sup>1</sup> · Zohreh Mirjafary<sup>2</sup>

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## Abstract

In order to examine the acidity of organic sulfuric acid derivatives in gas phase, comprehensive density functional theory (DFT) calculations at B3LYP/6-31++G(d,p) level have been undertaken. In the title compounds, one of the oxygen atoms is substituted by an 1,3-cyclopentadiene group. The focus of this paper is on DFT studies of two classes of sulfuric acid derivatives: dithionic and peroxydisulfuric acids. Tautomers of proposed organic sulfuric acids are also investigated. DFT calculations indicate that the acidity of the proposed acids without any electron withdrawing groups on the ring was more than sulfuric acid.

**Keywords** Dithionic acid · Peroxydisulfuric acid · Organic superacid · NICS data · HOMA index

## Introduction

Acidity is defined as ability of a compound to lose  $H^+$ , resulted negative charge. Proton transformation has great importance in different chemical and biochemical process [1]. Superacids are very useful chemicals in organic synthesis and material sciences such as alkylation, acylation, isomerization, polymerization, cracking, and coal industrial [2–4]. Superacids are used widely for preparation of carbocations which are important intermediates in organic synthesis. A magic acid (a mixture of Lewis and Brønsted acid) are also utilized for stabilization of unstable carbocations [5]. Generally, a superacid has greater acidity than 100% pure sulfuric acid [6]. Remarkable investigations by computational chemists have been made to tailor neutral small organic molecules as superacid [7–15]. The key point for design and fabrication of superacids is stabilization of the corresponding conjugate base in order to make the anion less basic. Four methods are utilized in the literature for design of a superacid: (1) delocalization of negative charge by substituent effects such as field/inductive and  $\pi$ -electron resonance effects [16, 17], (2) increasing of polarizability by using superacceptor groups [18], and (3) strong

hydrogen bonds in the conjugate base [19]. The fourth one is based on aromatic stabilization of negative charge in the corresponding conjugate bases. Recently, acidity of some organic Brønsted superacids bearing cyclopentadiene and polycyclic aromatic hydrocarbon derivatives with electron withdrawing groups such as -CN and -F has been investigated by researchers [8, 20–24]. The reported  $\Delta H_{acid}$  values for the strongest superacids bearing cyclopentadiene are about 220–275 kcal/mol.

Sulfuric acid,  $H_2SO_4$ , is the mostly used and central substance in chemical industries [25, 26] and it is an important reagent in chemical laboratories too. Sulfuric acid reacts with most chemicals to result the corresponding sulfate. In the present study, new protocol is used to design of the strongest neutral organic acid based on two classes of sulfuric acid derivatives: dithionic **1** and peroxydisulfuric acid **2** (Fig. 1). Replacing an oxygen atom doubly bonded to sulfur atom on these acids with cyclopentadiene leads to new small interesting organic compounds which can behave as superacids. The present strategy for design of highly acidic molecules involves stabilization of negative charge in the corresponding conjugate anions through strong intramolecular hydrogen bond and making aromaticity.

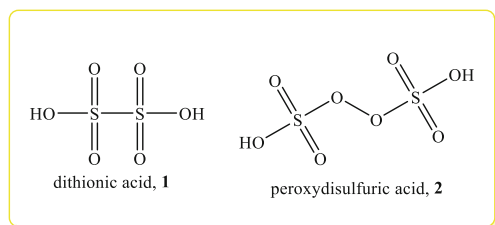
✉ Hamid Saeidian  
Saeidian1980@gmail.com

<sup>1</sup> Department of Science, Payame Noor University (PNU), P.O. Box: 19395-4697, Tehran, Iran

<sup>2</sup> Department of Chemistry, Tehran Science and Research Branch, Islamic Azad University, Tehran, Iran

## Computational details

Geometry optimizations and frequency calculations for all proposed molecules were performed by the use of Gaussian 09 program [27]. DFT calculations with the Becke three-



**Fig. 1** General structure of dithionic **1** and peroxydisulfuric acid **2**

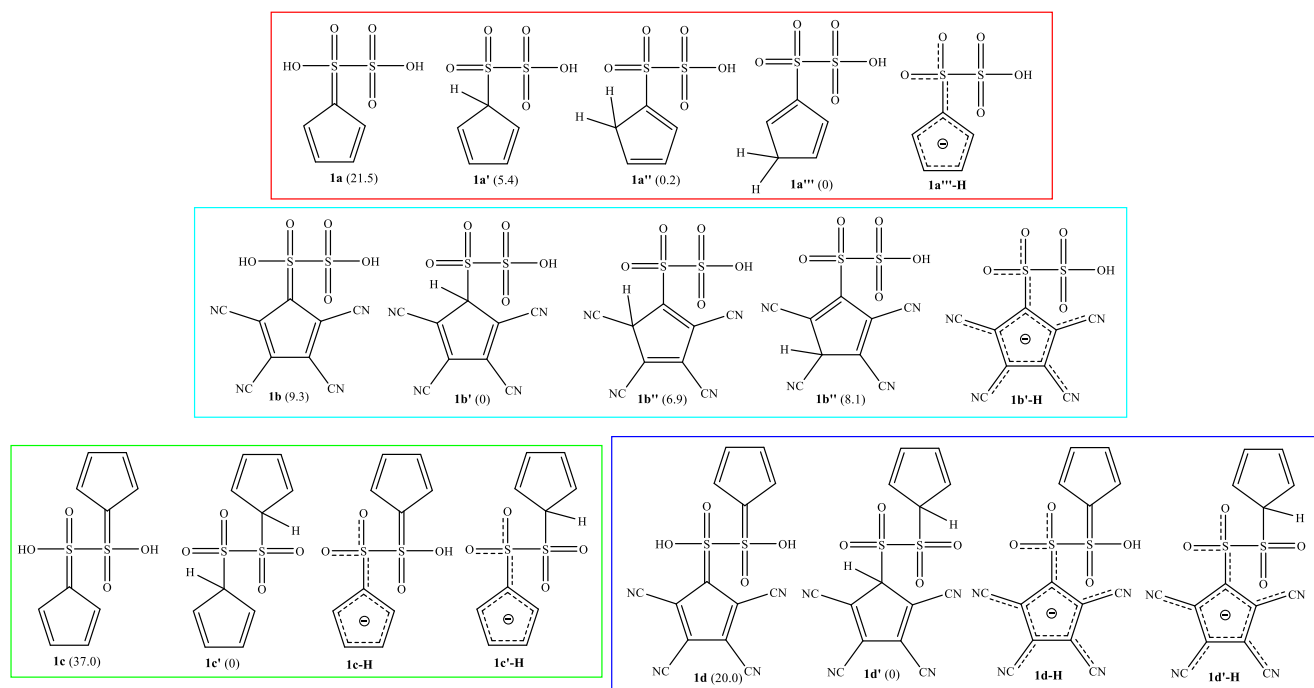
parameter hybrid functional (DFT-B3LYP) were performed, using 6-31++G(d,p) basis set. It has been demonstrated that DFT and its hybrid B3LYP functional [28, 29] gives a satisfactory description of the deprotonation process. There are many benchmark studies confirming the accuracy and reliability of DFT/B3LYP [30, 31]. Bryantsev and co-workers [31] compared the performances of different methods including MP2, B3LYP, X3LYP, and M06-L. They found that M06-L

gives more accurate results for neutral systems while B3LYP exhibits more accurate energies for systems including ions. As one of our goals is to find an accurate method that is computationally efficient, we have also focused on MP2 with 6-31++G(d,p) basis sets. Three studied molecules (Table 1) were optimized using MP2 method. The geometrical parameters of the molecules obtained by the MP2 and B3LYP were compared in Table 1. Comparison of the geometrical parameters reveals that the results obtained by the two methods are in good accordance.

Deprotonation reaction enthalpy ( $\Delta H_{\text{acid}}$ ), Gibbs free energy ( $\Delta G_{\text{acid}}$ ), nucleus-independent chemical shift (NICS) [32, 33], and the harmonic oscillator model of aromaticity (HOMA) index [14, 34] of the studied compounds can be considered as trustable parameters to compare the acidity of the chemicals and stability of the corresponding conjugated bases.

**Table 1** Calculated structural parameters for the B3LYP/6-31++G(d,p) and MP2/6-31++G(d,p) of five studied molecules

Molecule	Bond lengths (Å)	Calculated method	
		B3LYP	MP2
<p style="text-align: center;"><b>1a''</b></p>	$^4\text{S}=\text{O}^8$	1.464	1.466
	$^4\text{S}-\text{C}^7$	1.746	1.733
	$^{13}\text{H}-\text{C}^9$	1.098	1.094
	$^{12}\text{C}-\text{C}^7$	1.358	1.361
	$^{12}\text{C}-\text{C}^{11}$	1.454	1.457
<p style="text-align: center;"><b>1a'''-H</b></p>	$^4\text{S}=\text{O}^8$	1.474	1.474
	$^4\text{S}-\text{C}^7$	1.687	1.627
	$^{13}\text{H}-\text{C}^9$	1.081	1.080
	$^{12}\text{C}-\text{C}^7$	1.438	1.432
<p style="text-align: center;"><b>1b</b></p>	$^4\text{S}-\text{O}^8$	1.624	1.621
	$^4\text{S}-\text{C}^7$	1.706	1.679
	$^{18}\text{H}-\text{O}^8$	0.978	0.980
	$^{19}\text{N}=\text{C}^{16}$	1.163	1.189



**Scheme 1** The chemical structure of the proposed organic dithionic acids, C-H tautomers along their relative energies in kcal/mol (in parenthesis) as well as their conjugated base

**Table 2** The calculated  $\Delta H_{\text{acid}}$ ,  $\Delta G_{\text{acid}}$ , NICS (1), and HOMA values for organic dithionic acids

Compound	$\Delta H_{\text{acid}}^{\text{a}}$	$\Delta G_{\text{acid}}^{\text{a}}$	NICS(1) <sup>b</sup>	HOMA
<b>1a</b>	284.0	279.2	−2.1	0.47
<b>1a'</b>	301.2	293.3	−3.9	−0.92
<b>1a''</b>	305.4	298.1	−5.3	−0.49
<b>1a'''</b>	305.6 (298.5) <sup>c</sup>	298.3 (291.2) <sup>c</sup>	−5.1	−0.50
<b>(1a'''-H)<sup>-</sup></b>	–	–	−7.9	0.62
<b>1b</b>	247.8	240.8	−8.8	0.64
<b>1b'</b>	257.2	250.2	−5.2	−0.77
<b>1b''</b>	250.3	243.3	−5.7	−1.27
<b>1b'''</b>	249.0 (273.3) <sup>c</sup>	242.3 (265.9) <sup>c</sup>	−4.9	−1.3
<b>(1b'''-H)<sup>-</sup></b>	–	–	−9.7	0.75
<b>1c</b>	286.0 (376.5) <sup>d</sup>	280.1 (370.6) <sup>d</sup>	−5.9	0.21
<b>1c'</b>	309.1 (389.7) <sup>d</sup>	301.5 (382.4) <sup>d</sup>	−2.6	−0.93
<b>(1c-H)<sup>-</sup></b>	–	–	−6.2	0.48
<b>(1c'-H)<sup>-</sup></b>	–	–	−7.6	0.63
<b>1d</b>	258.8	253.3	−5.6	0.68
<b>1d'</b>	265.1	257.1	−4.2	0.59
<b>(1d-H)<sup>-</sup></b>	–	–	−10.5	0.74
<b>(1d'-H)<sup>-</sup></b>	–	–	−11.2	0.75

<sup>a</sup> kcal/mol, at 298.15 K and in gas phase

<sup>b</sup> Calculated at GIAO- B3LYP/6-31++G(d,p) level and in ppm

<sup>c</sup> For O-H deprotonation

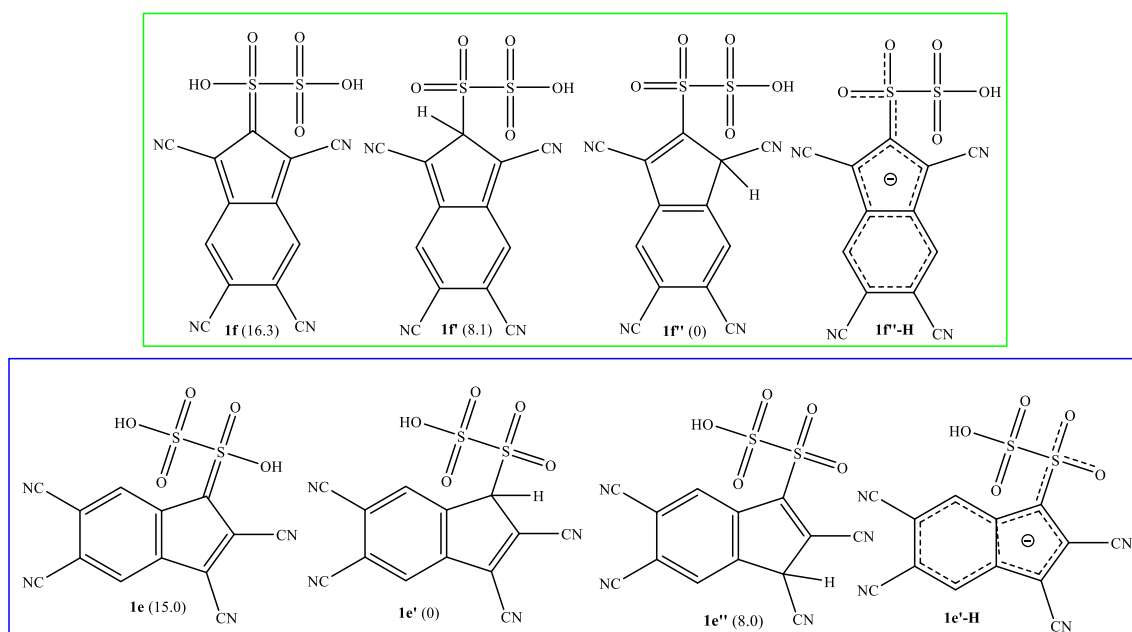
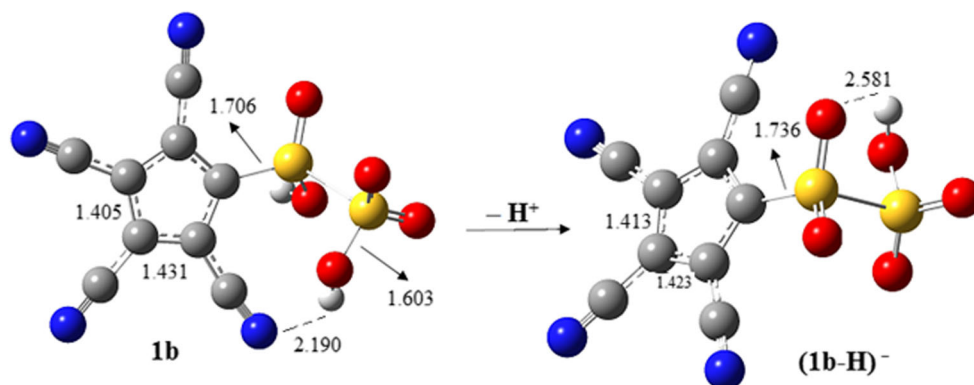
<sup>d</sup> For second deprotonation

## Results and discussion

Scheme 1 shows chemical structure of dithionic acid derivatives of cyclopentadiene and their corresponding conjugated bases. After deprotonation, the negative charge of the base is delocalized in the five membered ring and so it is expected more aromaticity than their corresponding acids. The aromaticity parameters, NICS and HOMA indices of the acids, and their conjugated bases are inserted in Table 2. As shown in Scheme 1, different dithionic acid derivatives as well as the corresponding prototropic tautomers were considered with their relative energies in kcal/mol. C-H tautomers are more stable than the corresponding dithionic acid derivatives. It is worthy to note that gas-phase acidity of the tautomers reduces by 0.2–20 kcal/mol than dithionic acid derivatives (Table 2). The calculated  $\Delta H_{\text{acid}}$  and  $\Delta G_{\text{acid}}$  data of dithionic acid derivatives and their prototropic tautomers are collected in Table 2. The NICS values for these acids are generally between −2.1 and −8.8 ppm, while these values for their conjugate bases are in the range of −6.2 to 11.2 ppm. The HOMA indices of the corresponding conjugate base of dithionic acid derivatives **1** are in the range of 0.48–0.75.

Replacing a (=O) group of dithionic acid with a cyclopentadiene motif resulted stable small organic acids (**1a-a'''**), in which **1a** shows  $\Delta H_{\text{acid}} = 284.0$  kcal/mol, that is 27.5 kcal/mol lower than that of  $\text{H}_2\text{SO}_4$  ( $\Delta H_{\text{acid}} = 311.5$  kcal/mol) [35].

**Fig. 2** The optimized structure of **1b** and **(1b-H)<sup>-</sup>**. The bond distances and angles are in (Å)



**Scheme 2** The dithionic acids bearing indene group, prototropic C-H tautomers and their relative energies in kcal/mol

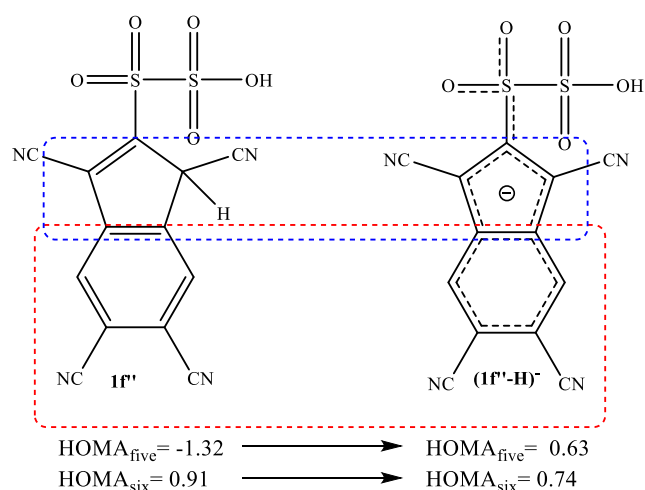
**Table 3** The calculated  $\Delta H_{\text{acid}}$ ,  $\Delta G_{\text{acid}}$ , HOMA,  $\text{NICS}_{\text{five}}(1)$ , and  $\text{NICS}_{\text{six}}(1)$  data for dithionic acids bearing 1*H*- and 2*H*-indene ring

Compound	$\Delta H_{\text{acid}}^{\text{a}}$	$\Delta G_{\text{acid}}^{\text{a}}$	$\text{NICS}_{\text{five}}(1)^{\text{b}}$	$\text{NICS}_{\text{six}}(1)^{\text{b}}$	HOMA <sup>c</sup>
<b>1e</b>	253.7	246.8	-5.7	-10.5	0.32 (0.87)
<b>1e'</b>	268.7	261.3	-4.2	-9.7	-0.85 (0.91)
<b>1e''</b>	260.7	253.9	-4.3	-10.4	-1.39 (0.91)
<b>(1e'-H)<sup>-</sup></b>	-	-	-10.6	-10.7	0.43 (0.76)
<b>1f</b>	246.9	240.2	-10.4	-9.4	0.53 (0.63)
<b>1f'</b>	255.1	248.0	-3.6	-2.9	-0.63 (0.30)
<b>1f''</b>	263.2	256.2	-4.3	-10.3	-1.32 (0.91)
<b>(1f''-H)<sup>-</sup></b>	-	-	-12.1	-9.5	0.63 (0.74)

<sup>a</sup> kcal/mol, at 298.15 K and in gas phase

<sup>b</sup> Calculated at GIAO-B3LYP/6-31++G(d,p) level and in ppm

<sup>c</sup> In parenthesis for six membered ring



**Scheme 3** HOMA index of five and six membered rings in  $(\mathbf{1f}'\text{-H})^-$  in comparing to  $\mathbf{1f}'$

These findings prompted us to investigate effect of cyano substituents on stabilization of conjugate base. Cyano motif has an electron-accepting nature and requires very less steric conditions for keeping of negative charge of conjugate base [35]. DFT calculations show that all isomers in category (b) exhibit strong acidity to superacid behavior,  $\Delta H_{\text{acid}} = 247\text{--}257$  kcal/mol. After deprotonation of (b), the negative charge is in the resonance with the strong electron-accepting  $-\text{CN}$  groups. Sharply increasing of HOMA index for the conjugate bases of (b), comparing to the corresponding acids supports this point. Substituting four  $-\text{CN}$  groups into organic acid  $\mathbf{1a}$ , gave superacid  $\mathbf{1b}$  with deprotonation enthalpy of 247.8 kcal/mol, 36.2 kcal/mol which is less than for  $\mathbf{1a}$ . This compound is more acidic than the most organic superacids which have been reported in literature. It should be noted that there are two different acidic hydrogens on the proposed organic dithionic acids ( $\mathbf{1b}'\text{-b}''$ ): C-H and O-H. DFT calculations on structure  $\mathbf{1b}''$  show that hydrogen on carbon is about 24.3 kcal/mol more acidic than hydrogen on oxygen. After deprotonation of these acids (C-H), it is expected an aromatic anion as the corresponding conjugate base and the negative charge is in the resonance with the strong electron-accepting cyano groups.

By more substituting cyclopentadiene group into dithionic acid  $\mathbf{1}$ , compounds  $\mathbf{1c}$  and  $\mathbf{1c}'$ , the acidity decreases a little and

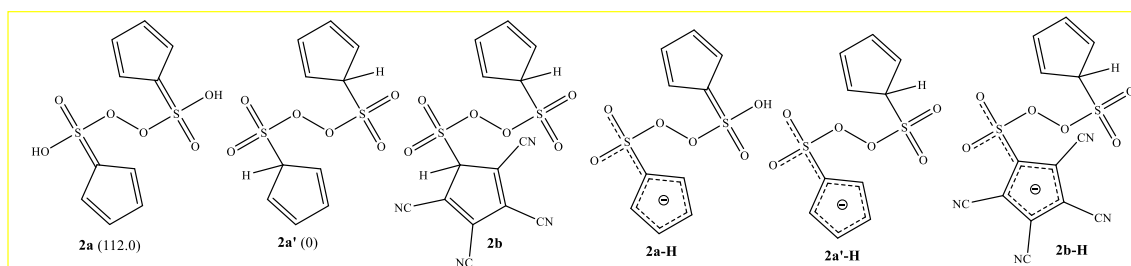
the calculated deprotonation enthalpy increases to 286 and 309.1 kcal/mol, respectively. As expected the second cyclopentadiene has no effect on delocalization of negative charge at the conjugate base. We carried out B3LYP/6-31++G(d,p) investigation on structure (d), in which two ( $=\text{O}$ ) groups of dithionic acid were replaced with two cyclopentadiene rings and one of the ring bears four  $-\text{CN}$  substituents. This strategy results in acidity enhancement comparing to category (c) and making aromaticity of  $(\mathbf{1d}'\text{-H})^-$  (Table 2). Tetracyano substituted cyclopentadiene facilitates the conjugation of  $\pi$ -electrons in  $(\mathbf{1d}'\text{-H})^-$  structure. Dramatic enhancement in the NICS index of  $(\mathbf{1d}'\text{-H})^-$  comparing to  $\mathbf{1d}$ , supports this result.

Compounds (c) and (d) have two same acidic hydrogens. They can donate proton twice. Enthalpy of the second deprotonation is more than the first one. The difference in deprotonation enthalpy for series (c) is about 80–90 kcal/mol (Table 2). The first conjugate base is capable of forming intra-hydrogen bond after losing  $\text{H}^+$  ion, making it more stable than the second conjugate base. Figure 2 compares the bond lengths of  $\mathbf{1b}$  and its conjugate base,  $(\mathbf{1b}\text{-H})^-$ . As shown, in the base form distance of  $\text{S}=\text{O}\cdots\text{HO}$  hydrogen bond is about 2.58 Å and partial charge on the H and O atoms are observed. Large and apposite charges make stronger hydrogen bond in short distance. After deprotonation, anion has a larger change in bond lengths than neutral acid (Fig. 2).

As mentioned in literature, the extension of conjugate system increases the acidity of poly enols [20]. So, a structure improvement of dithionic acid  $\mathbf{1}$  is made through replacing an oxygen atom, doubly bonded to sulfur with 1*H*- and 2*H*-indene which leads to new small organic compounds (e) and (f), respectively (Scheme 2).

The calculated  $\Delta H_{\text{acid}}$ ,  $\Delta G_{\text{acid}}$ , HOMA values for superacids (e) and (f), as well as  $\text{NICS}_{\text{five}}(1)$  and  $\text{NICS}_{\text{six}}(1)$  data are inserted in Table 3. The subscript of five and six show that NICS values were calculated at 1 Å above the five and six membered rings, respectively.

B3LYP/6-311++G(d,p) calculations on the tetrasubstituted structure of  $\mathbf{1e}'$  and  $\mathbf{1f}''$  (as stable tautomers) reveals that they exhibit strong acidity to superacid behavior,  $\Delta H_{\text{acid}} = 268.7$  and 263.2 kcal/mol, respectively. As shown in Table 3,



**Scheme 4** The chemical structure of the proposed organic peroxydisulfuric acids  $\mathbf{2}$ , C-H tautomer, their relative energies in kcal/mol as well as their conjugated base

**Table 4** The calculated  $\Delta H_{\text{acid}}$ ,  $\Delta G_{\text{acid}}$ , HOMA, and NICS (1) data for peroxydisulfuric acids **2** bearing two cyclopentadiene rings

Compound	$\Delta H_{\text{acid}}^a$	$\Delta G_{\text{acid}}^a$	NICS(1) <sup>b</sup>	HOMA
<b>2a</b>	213.5 (365.2) <sup>c</sup>	204.5 (356.2) <sup>c</sup>	−8.4	−0.87
( <b>2a-H</b> ) <sup>−</sup>	−	−	−10.0	0.76
<b>2a'</b>	310.0	303.8	−3.4	−1.04
( <b>2a'-H</b> ) <sup>−</sup>	−	−	−9.9	0.72
<b>2b</b>	265.7	258.2	−6.5	−0.83
( <b>2b-H</b> ) <sup>−</sup>	−	−	−10.9	−0.76

<sup>a</sup> kcal/mol, at 298.15 K and in gas phase<sup>b</sup> Calculated at GIAO- B3LYP/6-31++G(d,p) level and in ppm<sup>c</sup> For second deprotonation

dithionic acids bearing 1*H*-indene group (**e**) are more acidic than compound (**f**). It is interesting to note that HOMA index of five membered ring in (**1f''-H**)<sup>−</sup> was increased sharply in compared with its acid **1f''**; but reverse trend was observed in the HOMA index of six membered of (**1f''-H**)<sup>−</sup> and **1f''** (Table 3). The best way to explain this finding is comparing the structure of (**1f''-H**)<sup>−</sup> vs. **1f''**. Anion (**1f''-H**)<sup>−</sup> is a bicyclic aromatic hydrocarbon which its resonance stabilization energy per ring is less than that of **1f''**. Acid **1f''** has only an identifiable benzene ring and a five membered ring with an alkene bond which can not take part in  $\pi$ -electron delocalization. Therefore, HOMA index of six membered ring in (**1f''-H**)<sup>−</sup> was decreased in comparing to **1f''** (Scheme 3).

With these valuable results about organic dithionic superacid derivatives, attention was focused on peroxydisulfuric acid **2**. The chemical structure of the proposed organic peroxydisulfuric acids **2**, C-H tautomers, their relative energies in kcal/mol as well as their conjugated base are shown in Scheme 4. As shown in Scheme 4, C-H tautomer **2a'** is about 112 kcal/mol more stable than O-H tautomer **2a**.

The calculated  $\Delta H_{\text{acid}}$ ,  $\Delta G_{\text{acid}}$ , HOMA, and NICS values for acids peroxydisulfuric **2**, are provided in Table 4.  $\Delta H_{\text{acid}}$  for unsubstituted **2a** (less stable isomer) is 213.5 kcal/mol, showing a very strong superacid. It was seen that the acidity of **2a'** is increased by substituting cyano groups (4 CN) on cyclopentadiene ring, **2b**. DFT calculations show that  $\Delta H_{\text{acid}}$  value for tetracyano substituted **2b** is 265.7 kcal/mol (Table 4).

NICS and HOMA values for conjugate bases of peroxydisulfuric acids **2** in comparing to their acids were confirmed that the negative charge of the anions was delocalized well by the cyclopentadiene motif.

## Conclusion

In the present study, for the first time, two new class of organic dithionic and peroxydisulfuric acids as well as their some

prototropic tautomers containing cyclopentadiene motif was designed and their acidities were investigated by B3LYP/6-31++G(d,p) calculations in gas phase. Some of these proposed structures are more acidic than H<sub>2</sub>SO<sub>4</sub>, FSO<sub>3</sub>H, and even CF<sub>3</sub>SO<sub>3</sub>H. After deprotonation, the negative charge is delocalized in the aromatic cyclopentadiene group. NICS and HOMA indices of the corresponding conjugate base of the acids were also supported this finding. Substitution of electron withdrawing groups CN on aromatic rings, enhanced the acidity which fall into the defined range of superacidity.

## Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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