ORIGINAL RESEARCH

Design of organic superacids based on triflic and perchloric acid by using DFT-B3LYP calculations

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Abstract

Comprehensive density functional theory calculations at B3LYP/6-311++G(d, p) level have been undertaken on a new type of organic Brønsted acids based on perchloric and triflic acid in order to design superacids. The deprotonation enthalpy (ΔH_{acid}) and Gibbs free energy (ΔG_{acid}) were used to calculate the acidity of the proposed structures. For the acidity comparison, a systematic estimation of aromaticity in the superacids and their anions have been studied using structural (harmonic oscillator model of aromaticity) and magnetic (nucleus-independent chemical shift) criteria. The calculated gas phase ΔH_{acid} for the proposed acids were 319–249 kcal/mol which are less than the most mineral acids. Tautomers of proposed organic acids were also investigated.

Keywords DFT calculations · Superacid · Aromaticity · Perchloric acid · Triflic acid

Introduction

The protonation and deprotonation reactions are very important in the chemical and biochemical processes [1]. The acidity of a compound is usually defined as the proton loss and creation of an anionic species. The negative charge in the anion can be stabilized by various parameters such as the proper solvation. Due to low solubility, anion solvation is not successfully occurred in the most organic solvents. Hence, the acidity decreases sharply. The use of inorganic acids is severely restricted due to their corrosive properties and difficulty of working with them. Some organic syntheses involve processes in which the formation of carbocations is required. Carbocations are unstable species and very strong acids are required for their production and stabilization such as perchloric acid and trifluoromethanesulfonic (triflic) acid [2–4]. Superacids are used as effective catalyst in the organic syntheses such as alkylation, acylation, isomerization, polymerization, and coal industry [5]. A superacid is a compound with acidity greater than that of pure 100% sulfuric acid [6, 7]. Till now, many theoretical attempts have been made to design

the organic superacids [8–20]. Anion stability has been considered in most of the proposed methods. The negative charge on the conjugate base of the designed acid may be stabilized by electron-withdrawing substituents, resonance, and intramolecular hydrogen bonding [21–23]. Recently, our research team has been able to design the organic superacids based on fluorosulfuric, dithionic, peroxydisulfuric, and nitric acid, whose acidity falls in the range of the superacids [24–26]. In the continuation of these research works, the present study investigates acidity of the compounds (**a-f**) based on perchloric and triflic acid by using density functional theory (DFT).

Computational details

All geometric optimizations and frequency calculations for the all designed molecules have been carried out by using Gaussian 09 suite [27]. The DFT calculations have been performed using the B3LYP method in conjunction with 6-311++ G(d, p) basis set. Benchmarking the computational method is presented below. All structures were confirmed to be local energy minima by computing their analytical vibrational frequencies.

The deprotonation enthalpy (ΔH_{acid}) and Gibbs free energy (ΔG_{acid}) for the studied compounds in the gas phase

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Scheme 1 Schematic representation of the proposed superacids based on perchloric acid **a1-c7**, along with their anions. The numbers are relative energies of the isomers in kcal/mol
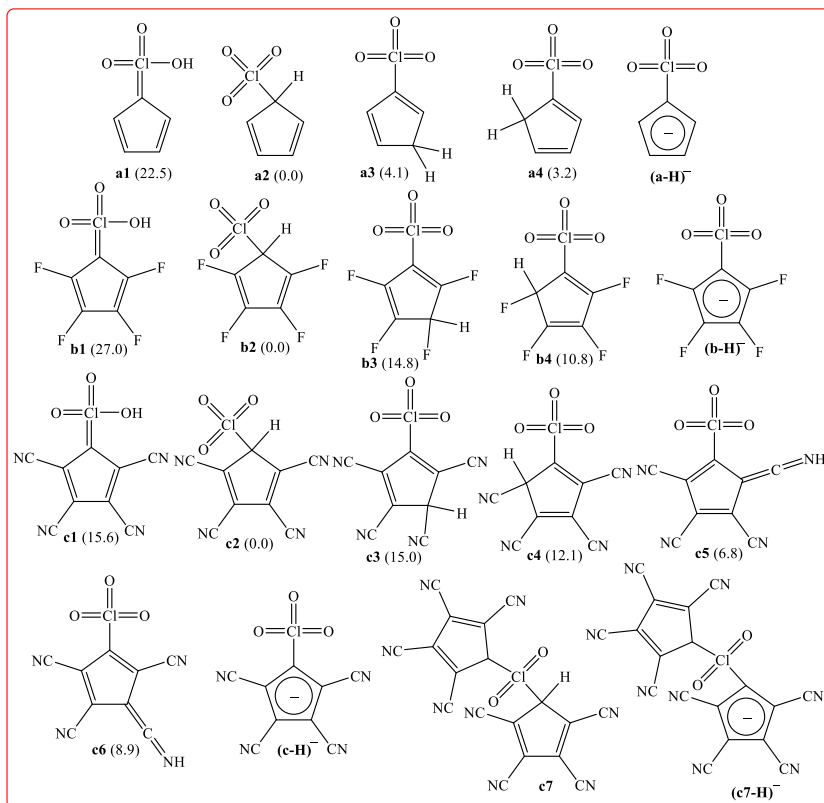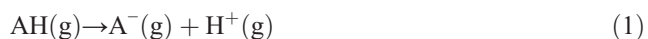

Scheme 2 Schematic representation of the proposed superacids based on triflic acid **d1-f8**, along with their anions. The numbers are relative energies of the isomers in kcal/mol
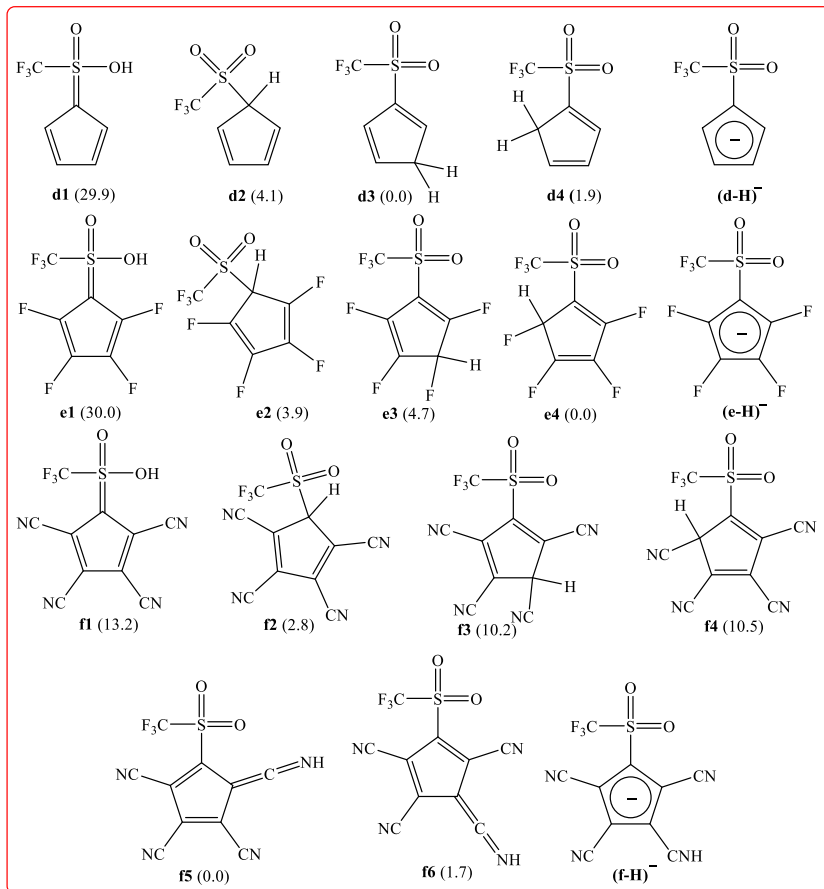
Scheme 3 Aromatization of cyclopentadienyl anion

As a planar molecule with 4n+2 π electrons Aromatic according Hückel rule
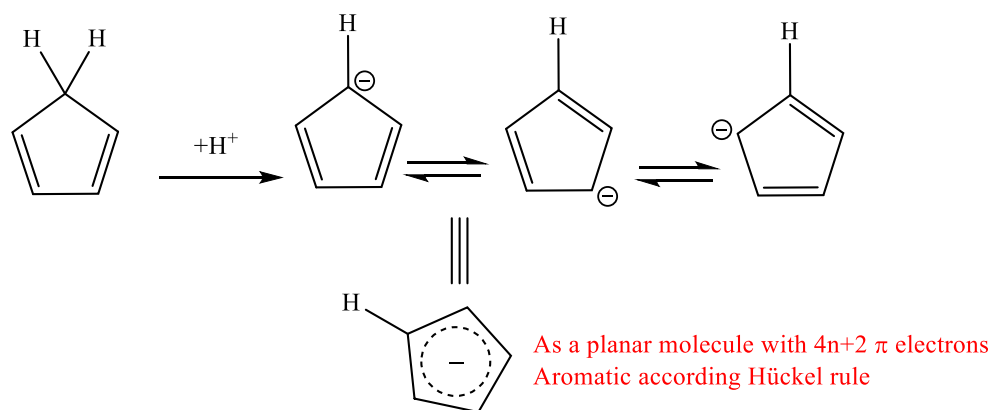
(reaction 1) can be considered as suitable and reliable parameters for comparing their acidities (Eqs. (1) and (2)).

$$AH(g) \rightarrow A^-(g) + H^+(g) \tag{1}$$

$$\Delta H_{acid} = H_{A^-} - H_{AH} + 1.48 \tag{2}$$

$$\Delta G_{acid} = G_{A^-} - G_{AH} - 6.27 \tag{3}$$

H and G in these equations describe the enthalpy and Gibbs free energy for the studied species at 298 K, respectively. The enthalpy and Gibbs free energy for proton (H^+) are given as 1.48 and − 6.27 kcal/mol, respectively.

Results and discussion

The strategy used to design the organic acids based on perchloric and trifluoric acid is to replace one of the oxygen atoms of perchloric and triflic acid with a vinyl cyclopentadiene (Cp) group (Schemes 1 and 2).

Upon deprotonation of the designed acids, the negative charge is expected to be placed on Cp. According to the Hückel rule, flat rings containing conjugated π bonds are aromatic in the case of having 4n+2 electrons. The negative charge on Cp makes it aromatic (Scheme 3) [3].

Table 1 Calculated ΔH_{acid} and bond lengths using the DFT, HF, and MP2 methods in conjunction with 6-311++G(d, p) basis set for **d1** and **(d-H)⁻**

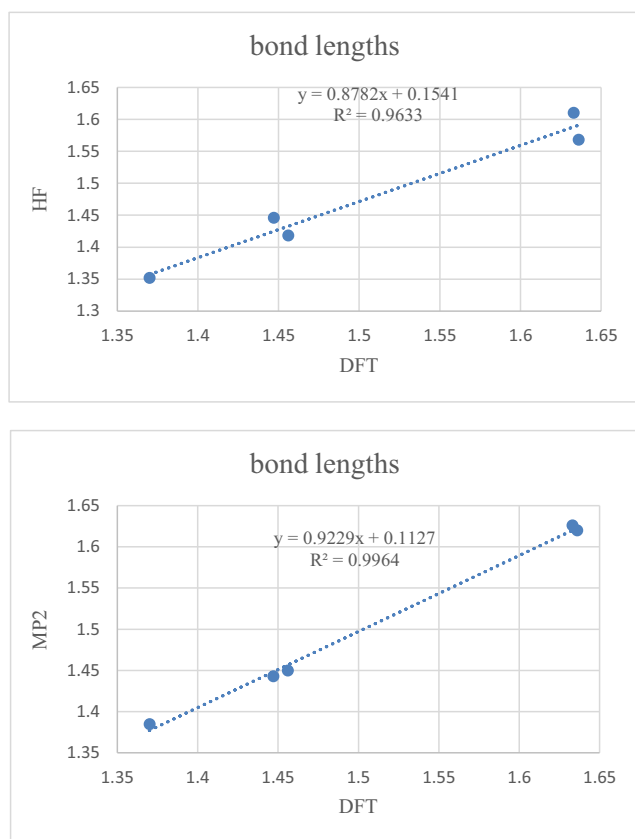| molecule	(Å) bond lengths	Calculated method			ΔH_{acid} (kcal/mol)		
		B3LYP	HF	MP2	B3LYP	HF	MP2
d1	C^2-S^4	1.633	1.610	1.626			
	O^7-S^4	1.456	1.418	1.450			
	C^2-C^1	1.447	1.446	1.443	287.89	287.27	284.92
	O^5-S^4	1.636	1.568	1.620			
	C^1-C^9	1.370	1.352	1.385			
(d-H)⁻	C^2-S^4	1.693	1.676	1.684			
	O^7-S^4	1.472	1.436	1.465			
	C^2-C^1	1.429	1.421	1427	-	-	-
	O^5-S^4	1.472	1.434	1.465			
	C^1-C^9	1.389	1.373	1.401			

Fig. 1 The linear regression between DFT *vs* HF and MP2-computed bond lengths

Evaluation of aromaticity for this ring in the designed acids relative to their conjugate bases can be another criterion for the acidity comparison. It is expected that the aromaticity indices of Cp increase in the anion with respect to its corresponding conjugate acid. Literature review illustrates that two significant and general indices are implemented for the aromaticity evaluation including (1) harmonic oscillator model of aromaticity (HOMA) [28, 29] and (2) nucleus-independent chemical shift (NICS) [30]. HOMA is a structural index which is defined for an all-carbon ring using Eq. (4) [31].

$$\text{HOMA} = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} \left(R_i - R_{\text{opt}} \right)^2 \tag{4}$$

In this relation, R_i and R_{opt} stand for the C–C bonds in the studied aromatic ring and benzene, respectively, which is estimated to be 1.388 Å for the later one. Also, n indicates the number of carbons in the studied ring and α as a normalization factor which is equal to 257.7. The NICS index as a *magnetic parameter* is also a reliable benchmark for determining the aromaticity of the studied compounds. The NICS value accounts for the negative magnetic coverage at the center of the ring and 1 Å above it. The negative value of NICS points out to the aromaticity. In this study, both HOMA and NICS indices have been calculated, compared, and discussed for the acid and the conjugate base.

Recently, we have successfully used B3LYP for calculating the PAs of some organic superacids [24–26]. Other studies

Table 2 The B3LYP/6-311++ G(d, p) calculated ΔH_{acid}, ΔG_{acid}, NICS (1) and HOMA data for organic perchloric acids **a1-c7**

Molecule	ΔH_{acid} (kcal/mol)	ΔG_{acid} (kcal/mol)	NICS (1, ppm)	HOMA
HClO$_4$	298.87	291.91	-	-
a1	300.00	294.67	− 2.78	0.34
a2	322.54	316.38	− 2.82	− 0.78
a3	318.48	312.49	− 5.18	− 0.92
a4	319.11	313.03	− 4.74	− 0.84
(a-H)⁻	-	-	− 9.84	0.87
b1	286.99	282.18	− 3.41	0.02
b2	314.05	308.48	− 3.21	− 0.79
b3	302.79	297.21	− 2.45	− 1.47
b4	306.84	301.81	− 4.16	− 1.32
(b-H)⁻	-	-	− 11.19	0.82
c1	251.04	246.00	− 7.97	0.65
c2	266.74	261.50	− 3.12	− 0.49
c3	251.68	246.51	− 4.43	− 1.38
c4	250.86	245.80	− 5.57	− 1.35
c5	259.85	254.63	− 9.21	0.65
c6	257.76	252.84	− 9.14	0.66
(c-H)⁻	-	-	− 10.31	0.81
c7	261.01	257.14	−6.21	0.26
(c7-H)⁻	-	-	−11.25	0.81
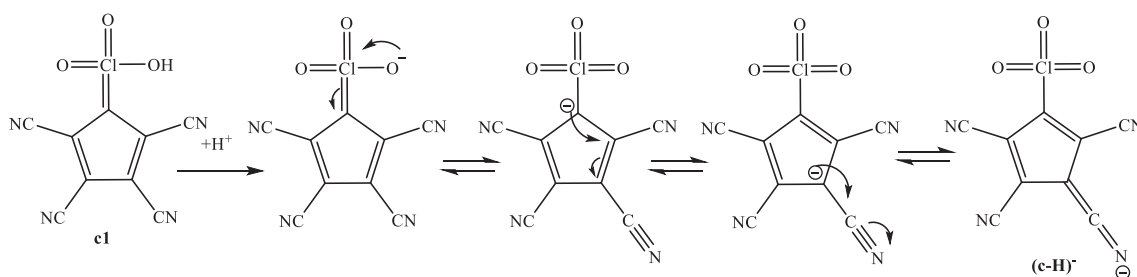
Scheme 4 The anion stabilization by cyanide groups

have employed B3LYP as appropriate methodology for predicting the acidity of organic acids [11, 32, 33]. It should be noted that one of the objectives of this study is to find a computationally accurate and reliable method; the structure of molecule **d1** and its anion **(d-H)**$^-$ have been investigated using DFT, HF, and MP2 methods with the same basis set of 6-311++G(d, p). Table 1 lists the selected bond lengths and acidity of molecule **d1**.

As can be seen from Table 1, the calculated bond lengths *via* the two methods of B3LYP and MP2 are close to each other with a slight difference. A plot of the DFT *vs* MP2-computed bond lengths (Fig. 1) shows a linear relationship with $r^2 = 0.996$. Besides, the obtained values of ΔH_{acid} *via* the three abovementioned methods are nearly identical for molecule **d1**. All the computations in this study were carried out using the DFT-B3LYP method as

this method has increased in popularity due to the relatively high accuracy of the results compared with the relatively low computational cost.

As can be seen from Schemes 1 and 2, C–H tautomers can also be considered for the designed superacids **a-f** in addition of the O–H isomer. As would be observed, the O–H isomers are unstable compared with the C–H ones and meet higher acidity. The most stable tautomer among the superacids of **a-c** set is their isomer 2 (**a2**, **b2**, **c2**). In addition to O–H and C–H tautomers for superacids **c**, N–H ones can also be considered (**c5**, **c6**). These isomers are unstable than C–H ones to the amount of 7–9 kcal/mol. It is noteworthy that tautomerism is also possible in the superacids **d-f**. The remarkable point about the stability of superacids based on triflic acid is that they do not have particular order like the perchloric acid–based counterparts. Among the superacids of group **d**, the structure **d3**, **e4** in group **e**, and N–H tautomer (**f5**) in group **f** are more stable isomers.

Table 3 The B3LYP/6-311++G(d, p) calculated ΔH_{acid}, ΔG_{acid}, NICS (1) and HOMA data for organic triflic acids **d-f**

| Molecule	ΔH_{acid} (kcal/mol)	ΔG_{acid} (kcal/mol)	NICS (1, ppm)	HOMA
CF₃SO₃H	298.95	304.44	-	-
d1	287.89	280.89	− 8.26	0.42
d2	313.72	306.37	− 7.69	− 0.98
d3	315.97	308.82	− 5.58	− 0.85
d4	317.85	310.54	− 6.22	− 0.71
(d-H)⁻	-	-	− 9.21	0.73
e1	275.52	268.10	− 8.89	0.21
e2	303.62	295.22	− 5.93	− 1.02
e3	300.78	293.27	− 1.80	− 1.42
e4	305.54	297.81	− 5.37	− 1.28
(e-H)⁻	-	-	− 9.04	0.64
f1	249.26	242.25	− 9.94	0.65
f2	259.69	252.61	− 6.80	− 0.73
f3	251.98	245.27	− 4.89	− 1.32
f4	252.29	245.54	− 6.83	− 1.28
f5	262.5	255.40	− 8.03	0.58
f6	258.87	251.74	− 8.45	0.65
(f-h)⁻	-	-	−12.37	0.78
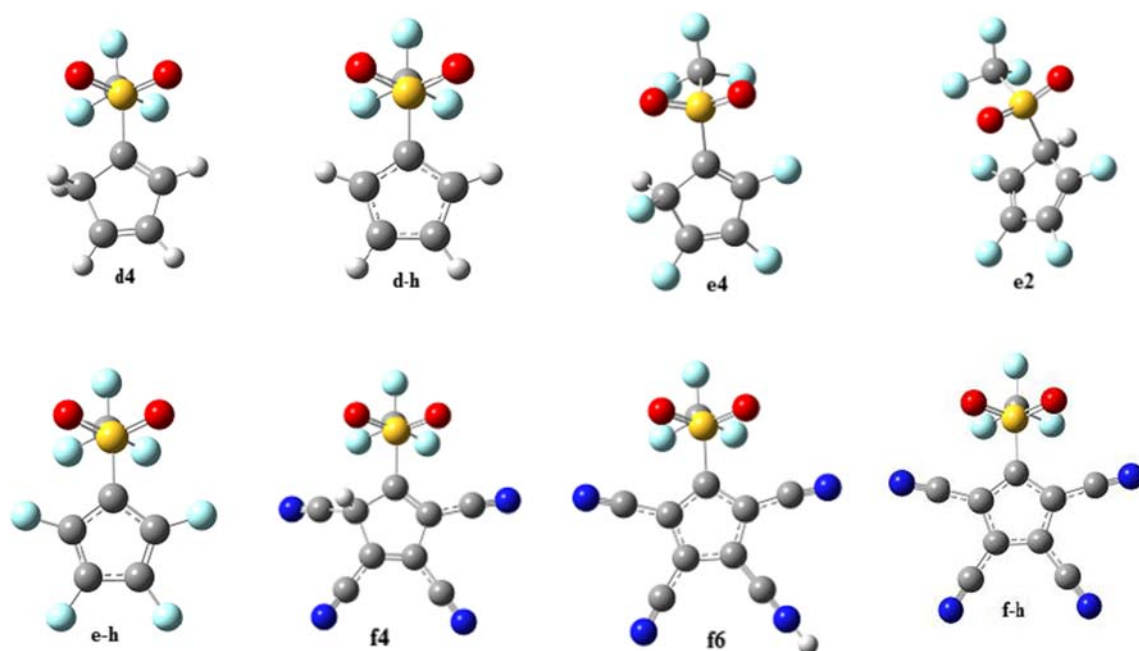
Fig. 2 Some optimized structures of to the organic superacids **d-f**

The data of ΔH_{acid}, ΔG_{acid}, NICS, and HOMA associated with the superacids **a1-c7** are given in Table 2.

Comparison of the acidity of molecule **a1** containing a Cp with that of perchloric acid shows that their acidities are approximately equal. The high acidity of **a1** is due to the stability of anion **(a-H)⁻**. Comparison of the aromaticity indices of the neutral molecules of group **a** with respect to their corresponding conjugate base ((a-H)⁻ anion) in Table 2 is a suitable criterion for the anion stability and basicity decrease of the conjugate base. As reflected in Table 2, the significant increase of HOMA and NICS indices confirms the formation of the aromatic cyclopentadienyl anion. The electronegative and electron-withdrawing substituents such as fluorine and cyanide group have the ability of stabilizing the negative charge through inductive and resonance effects. Placing 4 fluorine atoms in Cp increases the acidity of molecule **b1** relative to **a1** by 13.01 kcal/mol. Among the C-H

tautomers of the superacids of group **b**, molecule **b3** meets the highest acidity over the other ones. As illustrated by the aromaticity data in Table 2, the **(b-H)⁻** anion is more stable than the **(a-H)⁻** one and its NICS value is more aromatic to the amount of − 1.35 ppm. The fluorine atom possesses a high electronegativity, but due to its small atomic radius and the presence of 7 electrons in its valance layer, it has low electron-accepting capability, so it cannot stabilize the anion created by superacids as expected. The cyanide group is a unique group in terms of the electron acceptance, due to the sp hybridization of its carbon atom and binding to the electronegative nitrogen [34]. However, the important point about this group is the negative charge stability via resonance. As can be seen from Scheme 4, the negative charge is placed on the electronegative nitrogen through the resonance which leads to the anion stability as a consequence. The molecules in group **c** contain four
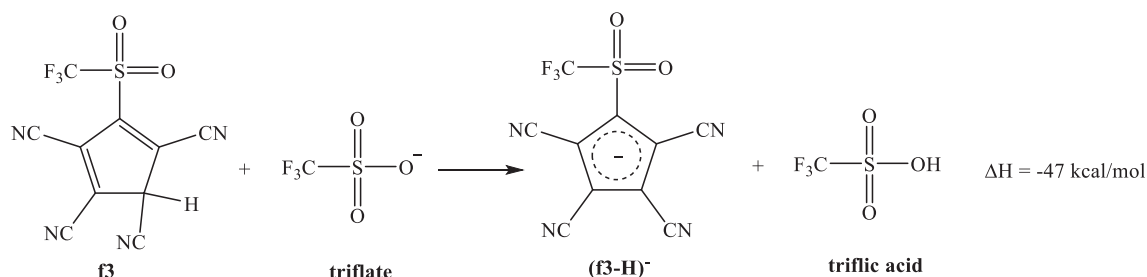
Scheme 5 The acidity of the acid **f3** relative to triflic acid

Scheme 6 The high NICS values for **d1**, **e1**, and **f1** derivatives in comparison to their conjugate bases
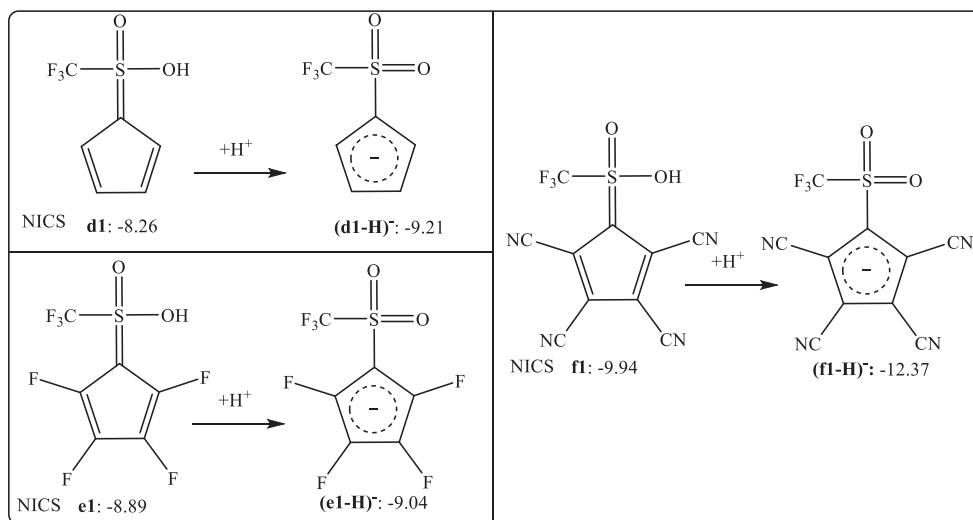
cyanide groups, with acidities far higher than those of groups **a** and **b**. Hence, all of this group's acids are considered as superacids and their protonated enthalpy (ΔH_{acid}) is below 266 kcal/mol and lower than that of perchloric acid to the amount 32 kcal/mol. The significant increase in NICS and HOMA data for Cp in the (**c-H**)⁻ anion relative to the neutral state indicates the complete negative charge stability.

Placing two Cp groups on perchloric acid creates superacid **c7** with $\Delta H_{acid} = 262.59$ kcal/mol. The comparison of **c7** molecule's acidity with that of the most stable isomer of group **c** (**c2**) indicates that adding Cp more than one case has negligible effect on their acidity. The superacid **c2** with small molecular size has acidity near that of **c7** molecule.

With these interesting and encouraging results, the acidic properties of triflic acid's derivatives containing a Cp have been examined by implementing the DFT-B3LYP/6-311++G(d, p) method and the obtained results are briefly presented in the following text. The acidity data and aromaticity indices are given in Table 3 for the organic triflic superacids **d-f**. Figure 2 illustrates some the optimized structure corresponding to the organic superacids **d-f**.

Placing a Cp group with a double bond on the triflic acid led to acid **d1** whose acidity is higher to the amount of 11.06 kcal/mol. Placing four fluorine atoms instead of the four hydrogen atoms of cyclopentadiene results into the molecules of group **e** with remarkable acidity. Further comparisons clarify that the acidity of similar isomers in this group is prominently higher than that of the perchloric acid–based acids. For example, the acidity of molecule **e1** is 11.47 kcal/mol higher than that of **b1**. Sharp increasing HOMA and NICS indices in the acids of group **e** indicates the complete stability of anion (**e-H**)⁻. The acidity amount highly increases by placing four CN groups in Cp. The remarkable point about the triflic acid–based superacids

containing cyanide group (**f**) is that the stable isomer in them is N–H tautomer (**f5**) which is more stable than O–H (**f1**) one to the amount of 13.2 kcal/mol. In the present study, **f1** is the strongest designed superacid with ΔH_{acid} as 249.26 kcal/mol, which is stronger than most of the superacids designed and reported within the scientific sources. The NICS value associated with Cp in (**f-H**)⁻ anion is equal to − 12.37 ppm which is higher than the standard value (− 10 ppm) for the benzene ring.

It should be noted that the acidity of the proposed structures relative to triflic acid can be reported using the reaction shown in Scheme 5. In this reaction, a negative data of ΔH means that **f3** is a stronger acid than triflic acid.

It is interesting to note that by carefully examining the NICS data, it was revealed that Cp in neutral superacids **d1**, **e1**, and **f1** derivatives has strong aromaticity. On the other hand, less changes were observed in NICS and HOMA data of them compared with their corresponding conjugate bases. In fact, the aromaticity indices have not notably increased in the corresponding anions (Scheme 6).
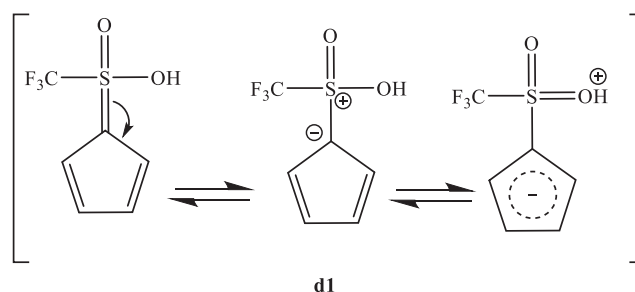
Scheme 7 Single bond between the sulfur and carbon atom in structures of **d1**, **e1**, and **f1** derivatives
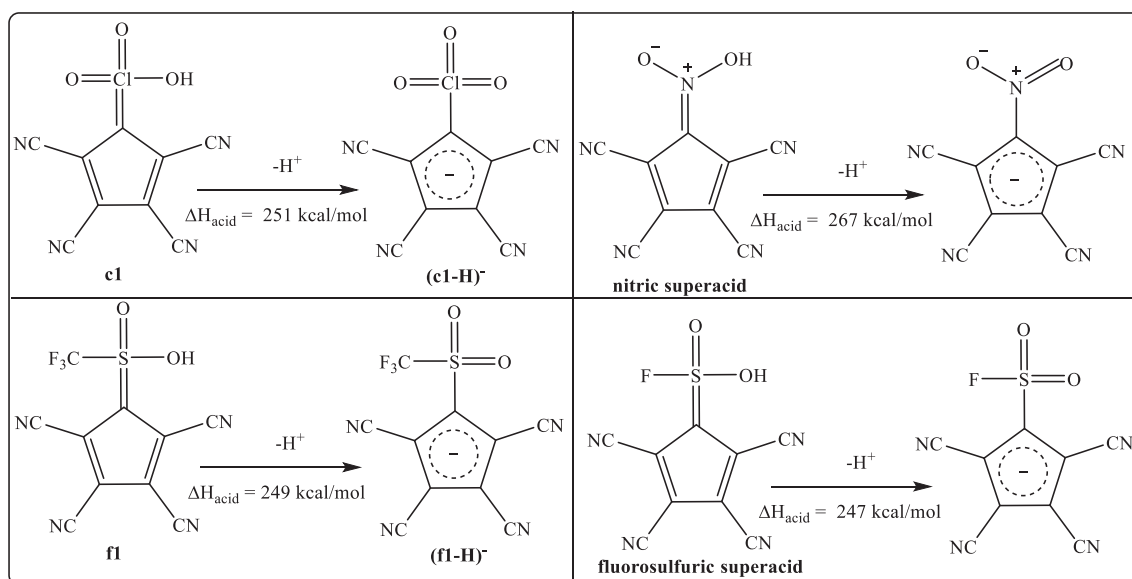
Scheme 8 Acidity comparison of organic superacids **c1** and **f1** with its analogues organo fluorosulfuric and nitric acid

One possible reason for the aromaticity index increment in the neutral form of these acids is the resonance phenomenon. The double bond between the sulfur and carbon atom in their structures is somewhat single bond (Scheme 7).

In order to prove and confirm this phenomenon, one can compare their bond length with the anion form in the optimized structures. In the case of such phenomena and resonance existence, there should be less change in the C–S bond length of their anion. Evaluating of these structures by GaussView software, indicates a slight increase in C–S bond length.

Conclusion

In conclusion, our protocol to superacids is to construct perchloric and triflic acid derivatives with one or two vinyl cyclopentadiene groups. Upon protonation of the molecules, the negative charge is delocalized in the aromatic cyclopentadienyl ring. The aromaticity of the 5-membered ring leads in stability of the conjugate bases. Both fluorine and cyanide groups on cyclopentadiene ring can be utilized as electron-withdrawing substituents that can stabilize the anions. The *deprotonation enthalpy* for most of the designed organic superacids **a-f** is smaller than 300 kcal/mol indicating that generally, they are stronger acids than the mineral acids. It should be said that the comparison of the designed compounds' acidity with organo fluorosulfuric derivatives [26] points out to the weaker acidity of the present derivatives while they are stronger acids than organonitric acids (Scheme 8) [24].

Compliance with ethical standards

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