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ORIGINAL RESEARCH

# Gas-phase acidities of organic acids based on 9H-fluorene scaffold: a DFT study

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## Abstract

The density functional theory (DFT) calculations have been performed on a new set of organic Brønsted acids based on 9H-fluorene scaffold. The optimal structures and acidity of the compounds have been calculated by using DFT/B3LYP/6–31 + +G(d,p) computational method. The acidity of the designed compounds was obtained in the range of 276–328 kcal/mol that the fluorene scaffold bearing ketenimine group **17** and trifilic group **20** with $\Delta H_{acid}$ of 276.3 and 285.4 kcal/mol, respectively, were found to be within the range of superacids, being more acidic than simple fluorene and mineral acids. The designed compounds and the corresponding conjugate bases were also examined from the aromaticity indices point of view. The tautomerization process for some designed structures was investigated by DFT calculations. Molecular electrostatic potential analysis for the designed acids and the corresponding conjugate bases was also used for charge distribution analysis.

**Keywords** Superacid · DFT calculation · Aromaticity · MEP map · Deprotonation

## Introduction

Chemists have long regarded inorganic acids such as sulfuric, nitric, perchloric and hydrofluoric acids as the strongest available acidic systems. This perspective significantly changed with the discovery of systems with an acidity of $10^{12}$ times higher than sulfuric acid [1]. Hall and Conant observed that weak organobases such as ketones and aldehydes could form salts with perchloric acid in nonaqueous solvents. Since perchloric acid can protonate such weak bases in nonaqueous systems, they called this acidic system as superacid [2]. Based on the researches of Gillespie et al., who have carried out pioneering activities in the field of mineral aspects of the acidic systems, all protic acids stronger than 100% sulfuric acid should be classified as superacids [3]. Therefore, $HClO_4$, $HSO_3F$, and $CF_3SO_3H$ are referred to as superacids. A superacid can be protonated by very weak bases such as methane, due to its very high acidity. The acidity threshold in the gas phase has been reported to be 300 kcal/mol [4]. Superacids and strong acids are used in cracking and alkylation processes and the chemical industry [5, 6]. The acidity of different acidic systems can be measured experimentally using UV–Vis and nuclear magnetic resonance spectroscopy [7, 8]. However, these experiments are typically performed in the solution phase, and the results are highly dependent on the properties of the solvent. In this regard, regardless of the type of solvent used, the gas-phase acidity has been presented as a standard method for identifying the superacid properties. The gas-phase acidity plays a significant role in the design of new superacids. Today, in computational chemistry, improving the acidity of organic compounds has attracted the attention of many researchers [9–19]. In most conducted studies, the negative charge on the corresponding conjugate base is stabilized by inductive effect (withdrawing groups), delocalization (aromaticity), and intramolecular hydrogen bonding [4].

The present research team has also conducted the DFT/B3LYP calculations on hybrid organic–inorganic acids to investigate their gas-phase acidity [20–23]. A strong acidity value was predicted for a set of fluorosulfuric acids in which oxygen is replaced by an unsaturated ring [23]. The acidity of these acids without the electron-withdrawing groups on the ring is greater than the fluorosulfuric acid. It was observed that the replacement of hydrogen by electron-withdrawing groups such as –CN and –F on the

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ring leads to an increment in the acidity up to the level of superacids.

Fluorene is a tricyclic aromatic hydrocarbon in which the five-membered ring has no aromaticity. It can be served as molecular scaffold for organic superacids. A salient structural feature of this compound is the central $C^9$(sp3)–H subunit, which can freeze the annulene network of the π bonds along the molecular framework. The C9-H site of the fluorene ring has a weak acidity ($pK_a$ = 22.6 in DMSO) whose protonation leads to forming of a stable aromatic anion with a bold orange color [24, 25]. According to the points mentioned above, and in continuation of previous works, the present study has attempted to design neutral organic superacids using fluorene scaffold and enole functional group and establish of substituents such as –F and –CN on the benzene rings (Scheme 1).

In the second section of the study, other acidic functional groups were placed on the C9-H site of the fluorene ring to obtain hybrid organic–inorganic acids (Scheme 2).

## Computational details

The geometric optimization and frequency calculations for all proposed structures have been carried out using Gaussian 09 software [26] and applying the DFT-B3LYP/6–31 + +G(d,p) computational method (Supporting Information). The frequency calculations were performed using the mentioned computational method to obtain the thermodynamic data of the deprotonation enthalpies ($\Delta H_{acid}$) and Gibbs free energies ($\Delta G_{acid}$) of the acids **1–23** (Eq. 1) at 298 K (Eqs. (2) and (3)) [23]:

$$AH(g) \rightarrow A^-(g) + H^+(g) \quad (1)$$

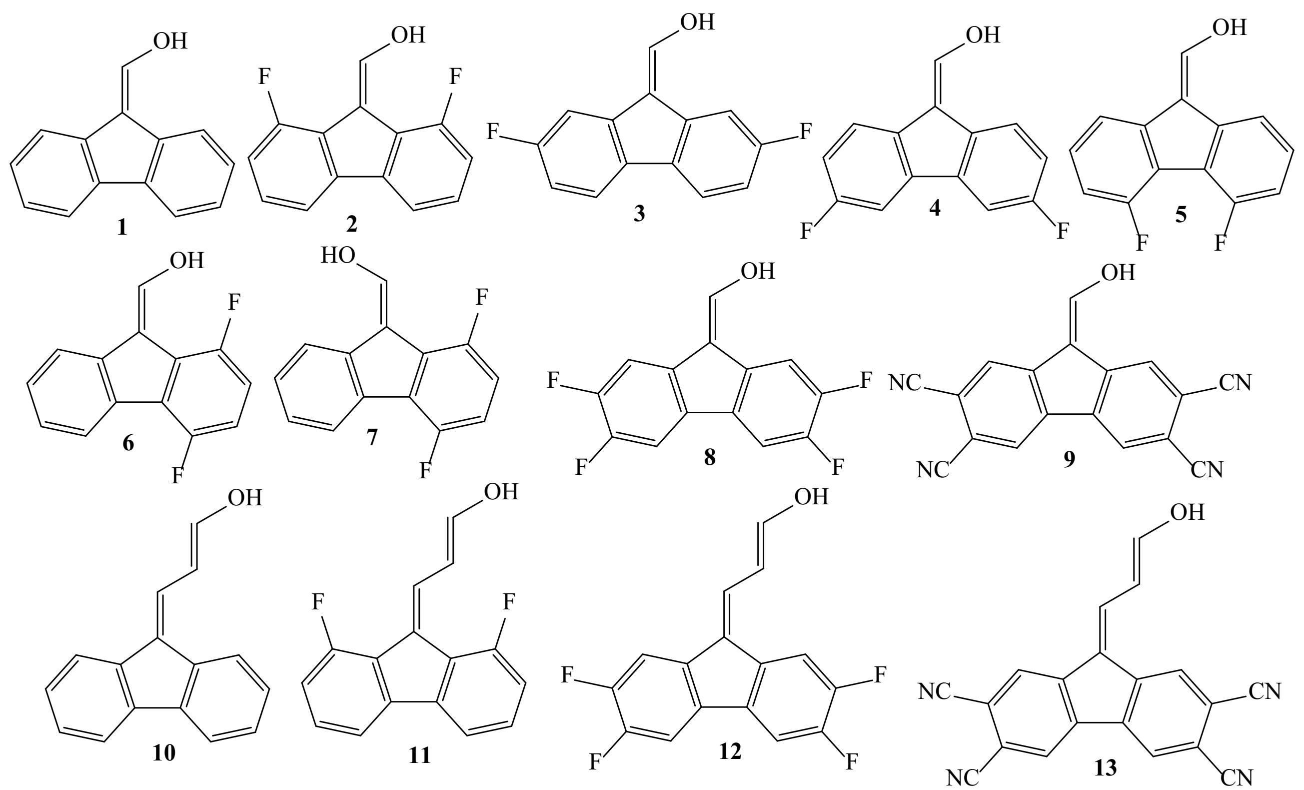
$$\Delta H_{acid} = H_{A^-} - H_{AH} + 1.48 \quad (2)$$

$$\Delta G_{acid} = G_{A^-} - G_{AH} - 6.27 \quad (3)$$

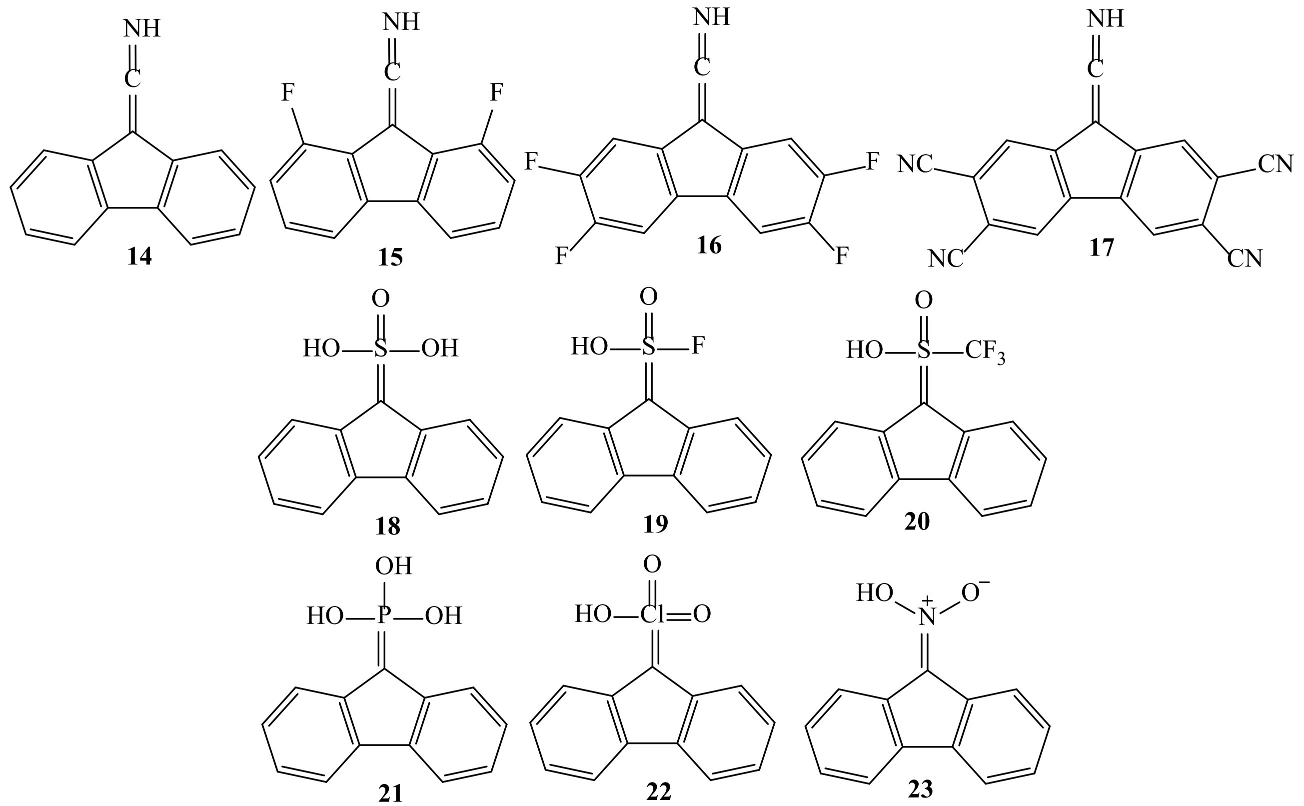
$H_{AH}$, $H_A{}^-$, $G_{AH}$, and $G_A{}^-$ donate enthalpies and Gibbs free energies of the designed acid and its corresponding anions, respectively. For the proton, the following values were used: $H_{298}(H^+)$ = 1.48 kcal/mol and $G_{298}(H^+)$ = −6.27 kcal/mol [27, 28]. Optimized coordinates, geometries, and energies of all structures are inserted in the Supporting Information.

## Results and discussion

Accuracy evaluation of computational method and the basis set used in the acidity estimation are of high prominence. Among the features of an ideal computational method, one can refer to the high computational speed and




**Scheme 1** The chemical structures of the proposed superacids bearing enole functional group




**Scheme 2** The chemical structures of the proposed superacids bearing acidic functional groups

cost-effectiveness and increased accuracy in the computational methods. It says that the DFT/B3LYP method usually leads to accurate results regarding the physicochemical properties of organic compounds such as protonation and deprotonation processes [29–31]. To find an accurate and computationally efficient method, the two computational B3LYP and MP2 methods have been compared in this study. For this purpose, the bond lengths and $\Delta H_{acid}$ associated with compound **1** have been calculated using the above two computational methods, and the results are presented in Table 1.

As would be observed, there is a relatively good agreement between the two methods. The plot of the calculated bond lengths obtained from the DFT method *vs* the calculated data from MP2 indicates a linear relationship with a regression value of $r^2 = 0.994$, as shown in Fig. 1.

The acidity of **1** was also calculated using the two mentioned methods, and the results showed that the enthalpy values were almost the same (Table 1). Therefore, the B3LYP/6–31 + + G(d,p) method is expected to be suitable for calculating the $\Delta H_{acid}$ of the designed acids **1–23**.

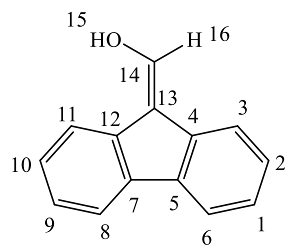
The prototropic tautomers of the chemicals **1**, **14,** and **18** are shown in Scheme 3 with their relative energies in kcal/mol. The C–H tautomers are more stable than the proposed structures in Schemes 1 and 2. In the present study, the structures in Schemes 1 and 2 were considered and their $\Delta H_{acid}$ were calculated by DFT calculations.

Some optimized structures of the examined compounds **1–23** at the B3LYP/6–31 + + G(d,p) computational level are shown in Fig. 2.

Usually, the strong acid is related to the more stable the resultant conjugate base (anion). Upon deprotonating the designed acids **1–23**, the negative charge is expected to be delocalized over the rings and reach stability. According to the Hückel's rule, placing of a negative charge on the cyclopentadiene ring in fluorene framework leads to its aromatization (Scheme 4). Therefore, the evaluation of aromaticity indices in corresponding conjugate bases is so essential. Aromaticity cannot be experimentally measured. Aromaticity is a phenomenon that can be described by different descriptors such as structural, energy, and magnetic properties.

The nucleus-independent chemical shift (NICS) [32] and harmonic oscillator model of aromaticity (HOMA) [33] are among the efficient methods for determining the aromaticity of cyclic compounds. The NICS parameter is calculated as the negative magnetic charge shielding at intervals in the center, top, and bottom of the ring. The NICS measurement at a distance of 1 Å above the ring using GIAO method [34] and bq dummy atom as a probe

**Table 1** Calculated bond lengths and $\Delta H_{acid}$ of **1** by using the DFT/B3LYP and MP2 methods with 6–31 + +G(d,p) basis set

| Molecule | bond lengths (Å) | Calculated method | | calculated ΔH acid (kcal/mol) | |
|---|---|---|---|---|---|
| | | B3LYP | MP2 | B3LYP | MP2 |
| | $C^{14}$- $H^{16}$ | 1.087 | 1.085 | | |
| | $C^{14}$- $O^{15}$ | 1.346 | 1.369 | | |
|  **1** | $C^{13}$- $C^{14}$ | 1.347 | 1.352 | 323.0 | 321.9 |
| | $C^{12}$- $C^{13}$ | 1.473 | 1.467 | | |
| | $C^{12}$- $C^{7}$ | 1.420 | 1.419 | | |
| | $C^{11}$- $C^{12}$ | 1.398 | 1.401 | | |

has been reported to be the best way to accurately determine the aromaticity characteristics. The negative and positive NICS values indicate the aromaticity and antiaromaticity natures of the examined compounds, respectively. HOMA index is a geometric descriptor of aromaticity based on the bond length. This index is calculated by using Eq. (4) [35].

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

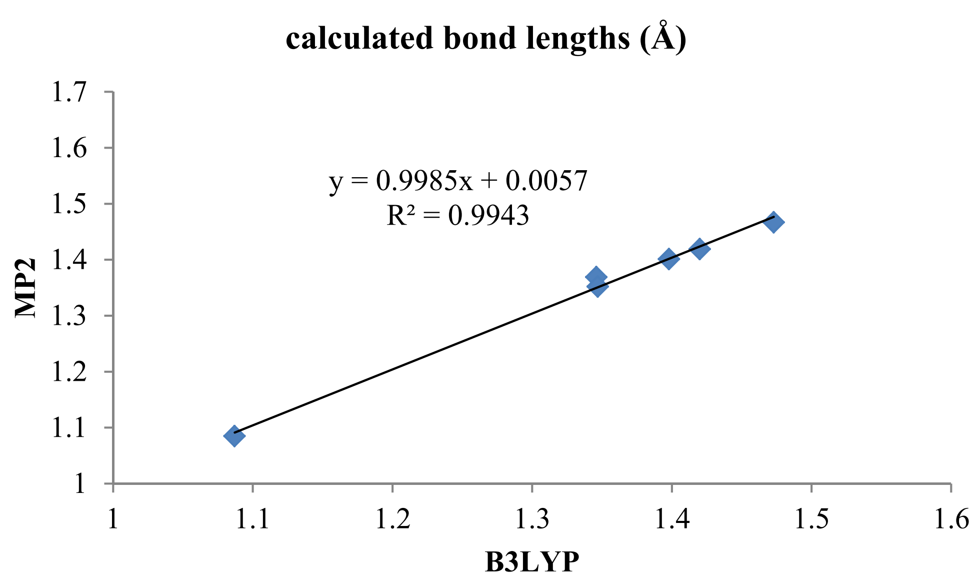
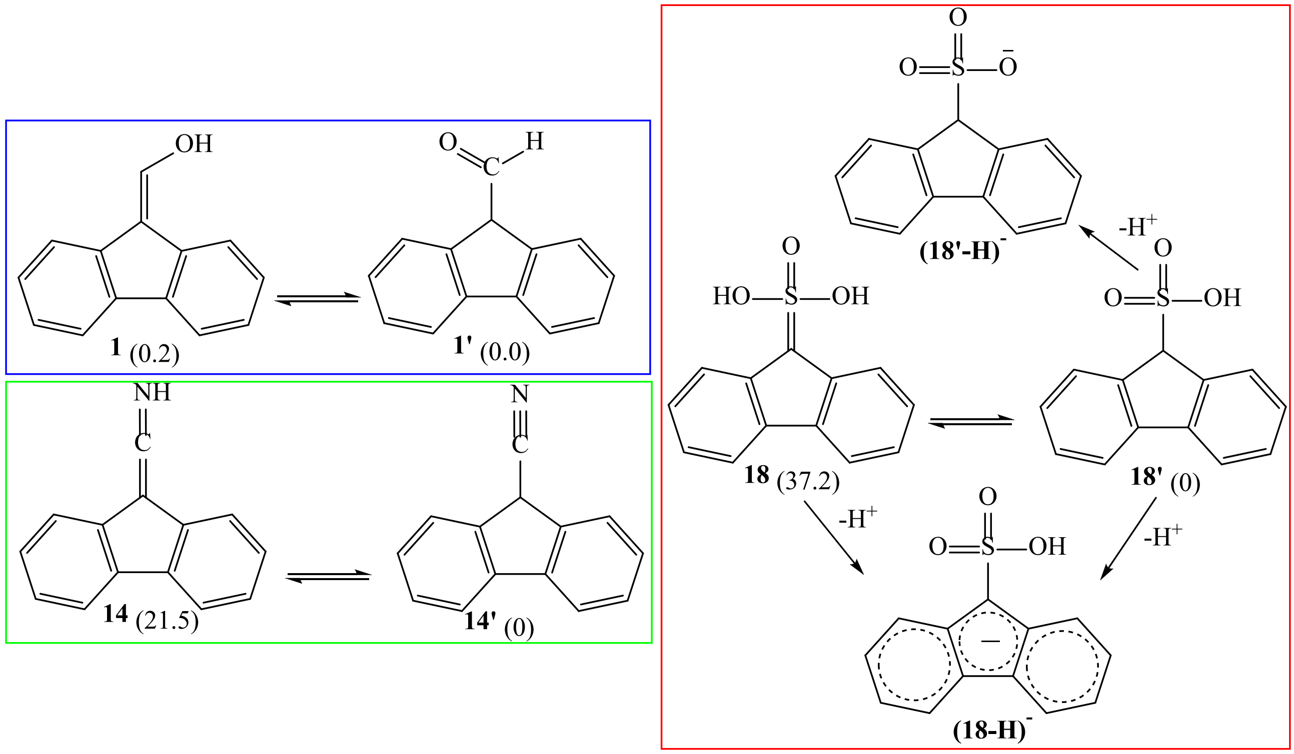



**Fig. 1** The linear regression between B3LYP calculated bond lengths and MP2 methods for **1**




**Scheme 3** Tautomerization of **1, 14**, and **18** and their relative energies in kcal/mol

Here, $n$ indicates the number of carbon atoms in the ring under study, and the normalization factor $\alpha$ is 257.7. In Eq. (3), $R_i$ and $R_{opt}$ stand for the length of C–C bonds in the investigated aromatic ring and an ideal aromatic system such as benzene, respectively. Krygowski reported the $d_{opt}$ value as equal to 1.388 Å for benzene [33]. On the other hand, the B3LYP/6–311 + G(d,p)-calculated $R_{opt}$ for ionic homoaromatic $C_5H_5^-$ is 1.415 [36]. It should be noted that HOMA is equal to 1 for the benzene ring, and the aromaticity of other compounds is compared with this value. The HOMA and NCIS values were calculated and reported for the studied compounds. Tables 2 and 3 present the values of $\Delta H_{acid}$,

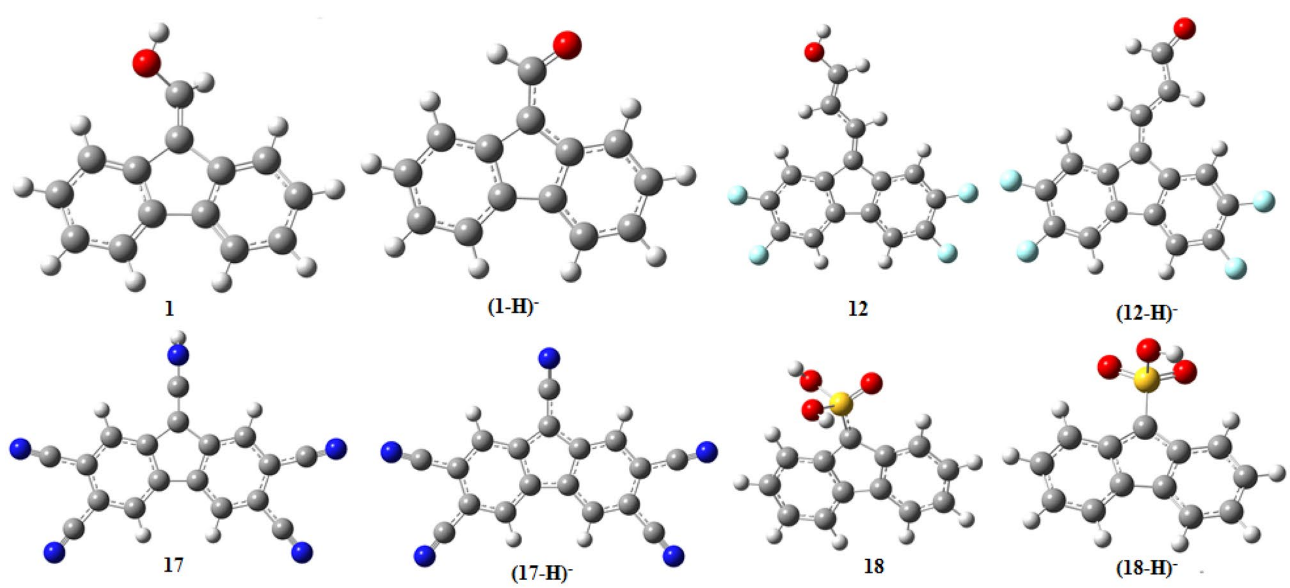
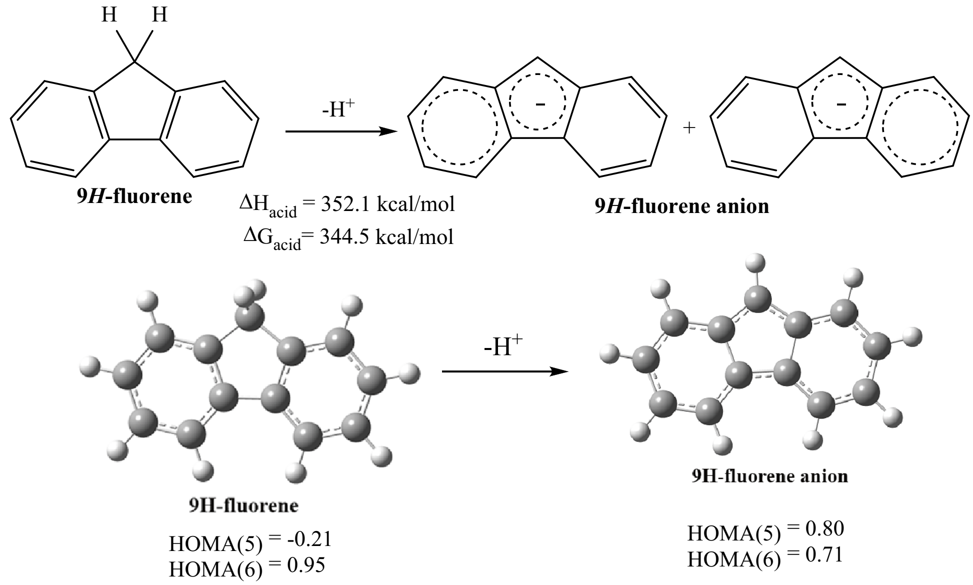



**Fig. 2** Some optimized structures of **1–23** and their corresponding conjugate bases at the B3LYP/6–31 + + G(d,p)

**Scheme 4** Deprotonation of 9H-fluorene results an aromatic system




$\Delta G_{acid}$, HOMA, and NICS associated with compounds **1–23** and their anions.

As mentioned above, the 9H-fluorene molecule is a weak acid. According to Scheme 4, this compound is converted to a stable anion by losing a proton. The HOMA and NICS values have been calculated for the five- and six-membered fluorene rings (Table 2). According to the estimated values, it can be observed that the five-membered ring is not aromatic in neutral form. Due to deprotonation, the HOMA and NICS values in the anionic form have significantly increased, indicating the aromatization of the five-membered ring and negative charge stability as well. It is also worth noting that the aromaticity indices of benzene rings in the anionic form are expected to decrease relative to the neutral one. The resonance energy of the molecule in the anionic form is distributed between all the rings. In contrast, in the neutral form, two separate benzene rings have their own energy. Comparing the aromaticity indices in the neutral and anionic forms of all studied compounds testifies to this point (Tables 2 and 3). Adding an enole group to the C9-H of the fluorene ring results in acid **1** with an acidity of $\Delta H_{acid}$ = 323.0 kcal/mol, which has more acidity than simple 9H-fluorene to amount of 29.1 kcal/mol. Placing fluorine atoms on the aromatic rings in different situations leads to compounds **2–8**. Compound **2** bearing two electronegative fluorine atoms on C1 and C8 has $\Delta H_{acid}$ = 328.2 kcal/mol while the acidity of **3** with two –F on C2 and C7 is $\Delta H_{acid}$ = 316.3 kcal/mol. Among the acids **2–8**, compound **3** is the strongest superacid which may be due to the proper symmetry of the compound and appropriate delocalization of the negative charge in its corresponding conjugate base. Replacing hydrogen on C3 and C6 with fluorine atoms at 9H-fluorene structure resulted in compound **4** with $\Delta H_{acid}$ = 318.2 kcal/mol that is 33.9 kcal/mol lower than 9H-fluorene. According to the data in Table 2, it is clear that compound **5** bearing fluorine atoms meets one of the highest acidities ($\Delta H_{acid}$ = 316.5 kcal/mol). The fluorine electron-withdrawing substituents are positioned in this compound in such a way that they meet maximum repulsion concerning to each other (Fig. 3). Therefore, compound **5** is unstable, and deprotonation has caused the aromaticity parameters of the five-membered ring to be significantly increased in the conjugate base of **5** and stabilized as well. Stability of the conjugate base **(5-H)**$^-$ due to the increased aromaticity leads to an improvement in the acidity of compound **5**.

Moreover, simultaneous placement of two fluorine atoms on a benzene ring in acid **6** has been investigated. It is observed that the acidity of this compound has increased compared to **2**; however, it is lower than that of compounds **3–5**. It should be noted that molecules **2** and **6** are relatively stable due to the formation of intramolecular hydrogen bonding between the –F and the –OH group and do not tend to lose proton (Fig. 4).

Compound **6** has an asymmetric structure, and the negative charge distribution is not uniform in it. Examination of HOMA indices in the three rings of five-membered one, benzene and benzene ring containing two –F atoms, shows that the stability of the five-membered ring has dramatically increased, while no significant change can be observed in the stability of the benzene rings. The negative charge in this molecule has a greater tendency to form resonance in the five-membered ring, and therefore, the HOMA index significantly increases. Compounds **6** and **7** are geometrical isomers to each other, ***Z*-6** and ***E*-7**. It was found that the formation of intramolecular hydrogen bonding between the –F atom and the –OH group in the ***Z*-6** isomer leads to a

**Table 2** The calculated $\Delta H_{acid}$, $\Delta G_{acid}$, HOMA, and NICS data for acids **1–13**

| Compound | $\Delta H_{acid}$[a] | $\Delta G_{acid}$[a] | NICS(1)[b] | HOMA |
|---|---|---|---|---|
| **Fluorene** | 352.1 | 344.5 | −1.87 | 0.21 (0.95)[c] |
| **(Fluorine-H)**$^-$ | - | - | −12.80 | 0.80 (0.71)[c] |
| **1** | 323.0 | 315.7 | −2.30 | 0.45 (0.93)[c] |
| **(1-H)**$^-$ | - | - | −8.95 | 0.78 (0.85)[c] |
| **1´** | 323.3 | 316.7 | −1.03 | 0.29 (0.95)[c] |
| **(1´-H)**$^-$ | - | - | −8.95 | 0.78 (0.85)[c] |
| **2** | 328.2 | 319.9 | −3.16 | 0.49 (0.93)[c] |
| **(2-H)**$^-$ | - | - | −9.38 | 0.77 (0.76)[c] |
| **3** | 316.3 | 308.9 | −2.25 | 0.49 (0.94)[c] |
| **(3-H)**$^-$ | - | - | −8.42 | 0.83 (0.84)[c] |
| **4** | 318.2 | 310.8 | −2.63 | 0.50 (0.94)[c] |
| **(4-H)**$^-$ | - | - | −9.24 | 0.80 (0.86)[c] |
| **5** | 316.5 | 309.1 | −2.54 | 0.50 (0.93)[c] |
| **(5-H)**$^-$ | - | - | −8.89 | 0.78 (0.83)[c] |
| **6** | 325.9 | 317.7 | −2.62 | 0.51 (0.93)[c] (0.84)[d] |
| **(6-H)**$^-$ | - | - | −11.76 | 0.80 (0.85)[c] (0.83)[d] |
| **7** | 319.0 | 311.5 | −2.62 | 0.54 (0.93)[c] (0.95)[d] |
| **(7-H)**$^-$ | - | - | −8.82 | 0.80 (0.85)[c] (0.83)[d] |
| **8** | 312.0 | 304.6 | −2.56 | 0.51 (0.95)[c] |
| **(8-H)**$^-$ | - | - | −8.98 | 0.81 (0.86)[c] |
| **9** | 287.2 | 279.9 | −3.91 | 0.46 (0.89)[c] |
| **(9-H)**$^-$ | - | - | −10.10 | 0.85 (0.77)[c] |
| **10** | 317.7 | 310.8 | −1.97 | 0.43 (0.94)[c] |
| **(10-H)**$^-$ | - | - | −7.69 | 0.74 (0.85)[c] |
| **11** | 316.9 | 309.5 | −2.91 | 0.44 (0.95)[c] |
| **(11-H)**$^-$ | - | - | −8.76 | 0.74 (0.86)[c] |
| **12** | 308.8 | 301.6 | −2.31 | 0.47 (0.96)[c] |
| **(12-H)**$^-$ | - | - | −8.11 | 0.77 (0.86)[c] |
| **13** | 287.3 | 280.0 | −3.98 | 0.56 (0.87)[c] |
| **(13-H)**$^-$ | - | - | −9.71 | 0.83 (0.75)[c] |

[a] B3LYP/6–31 + +G(d,p), kcal/mol, at 298 K

[b]Calculated at GIAO-B3LYP/6–31 + +G(d,p) level and in ppm

[c]For 6-membered ring

[d]For 6-membered ring bearing fluorine atoms

**Table 3** The calculated $\Delta H_{acid}$, $\Delta G_{acid}$, HOMA, and NICS data for acids **14–23**

| Compound | $\Delta H_{acid}$[a] | $\Delta G_{acid}$[a] | NICS(1)[b] | HOMA |
|---|---|---|---|---|
| **14** | 302.9 | 295.5 | −5.61 | 0.61 (0.92)[c] |
| **(14-H)**$^-$ | - | - | −10.85 | 0.83 (0.82)[c] |
| **14´** | 325.8 | 317.0 | −3.20 | 0.50 (0.96)[c] |
| **(14´-H)**$^-$ | - | - | −10.85 | 0.83 (0.82)[c] |
| **15** | 311.6 | 304.0 | −4.21 | 0.57 (0.94)[c] |
| **(15-H)**$^-$ | - | - | −11.04 | 0.85 (0.82)[c] |
| **16** | 303.0 | 294.5 | −3.92 | 0.53 (0.95)[c] |
| **(16-H)**$^-$ | - | - | −10.71 | 0.85 (0.96)[c] |
| **17** | 276.3 | 268.9 | −5.18 | 0.61 (0.88)[c] |
| **(17-H)**$^-$ | - | - | −11.27 | 0.87 (0.75)[c] |
| **18** | 291.9 | 285.0 | −4.91 | 0.92 (0.57)[c] |
| **(18-H)**$^-$ | - | - | −10.26 | 0.82 (0.84)[c] |
| **18´** | 313.0 | 305.9 | −2.26 | 0.21 (0.95)[c] |
| **(18´-H)**$^-$ | - | - | −10.26 | 0.82 (0.84)[c] |
| **19** | 286.8 | 279.8 | −3.03 | 0.51 (0.93)[c] |
| **(19-H)**$^-$ | - | - | −8.25 | 0.78 (0.82)[c] |
| **20** | 285.4 | 278.5 | −5.14 | 0.53 (0.93)[c] |
| **(20-H)**$^-$ | - | - | −9.52 | 0.78 (0.86)[c] |
| **21** | 303.9 | 296.4 | −6.74 | 0.62 (0.90)[c] |
| **(21-H)**$^-$ | - | - | −10.11 | 0.81 (0.82)[c] |
| **22** | 305.5 | 300.8 | −1.34 | 0.64 (0.92)[c] |
| **(22-H)**$^-$ | - | - | −10.33 | 0.75 (0.83)[c] |
| **23** | 317.9 | 310.7 | −1.63 | 0.58 (0.93)[c] |
| **(23-H)**$^-$ | - | - | −6.88 | 0.79 (0.87) |

[a]B3LYP/6–31 + +G(d,p), kcal/mol, at 298 K

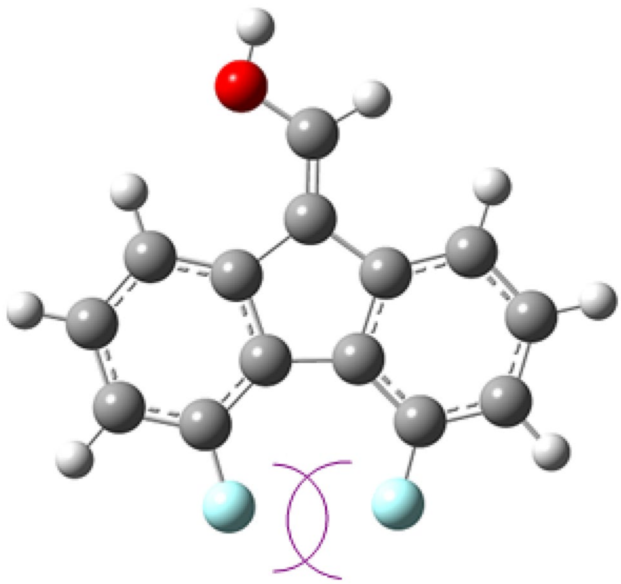
[b]Calculated at GIAO-B3LYP/6–31 + +G(d,p) level and in ppm

[c]For 6-membered ring

reduction in the acidity by about 6–7 kcal/mol. We carried out a computational investigation on structure **8** bearing four F atoms. Using four F atoms on benzene rings results in acidity enhancement to 312.0 kcal/mol for **8**. The fluorine atom is a strong electron-withdrawing group while having a low electron acceptor tendency due to its small atomic radius. The cyano group is an appropriate electron acceptor group. It needs less steric requirements for delocalization of negative charge of the corresponding conjugate base. The –CN groups can easily delocalize negative charge with resonance and inductive effect and increase the stability and consequently improve the acidity of the examined compounds and achieve strong acids. According to Table 2, it can be observed that the acidity of compound **9** has significantly increased by adding four cyano groups being higher than that of **1** to the amount of 36 kcal/mol. B3LYP/6–31 + +G(d,p) calculations reveal that compound **9** exhibits strong acidity to superacid behavior, $\Delta H_{acid}$ = 287.2 kcal/mol. The HOMA index in the conjugate base of **9** has increased by about 0.39, which increases the aromaticity of the five-membered ring and improves its acidity as a consequence.

The π system expansion usually results in better delocalization of negative charge throughout the molecule. Hence, a double bond was added to the enole structure of compound **1**. Contrary to expectations, a decrease in $\Delta H_{acid}$ was observed. However, adding four –CN electron-withdrawing groups to **10** has led to the formation of structure **13**, whose acidity has been estimated to be higher than that of the basic fluorene molecule to the amount of 65 kcal/mol and falls within the range of superacids [4].

The findings prompted us to investigate new superacids based on the strong inorganic acids of perchloric, sulfonic, nitric, and phosphoric acid (Table 3). Furthermore, the effect



5

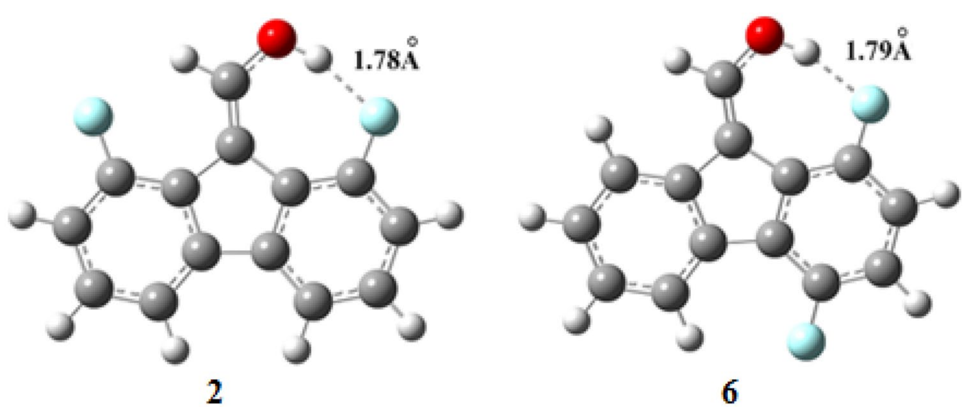
**Fig. 3** Repulsion between two fluorine atoms in structure of **5**

of adding C = C = NH substituent was investigated on the acidity of **14–17**. According to Table 3, it can be seen that adding the ketenimine group (–C = C = NH) has led to an increment in the acidity of compound **14** to the amount of 302.9 kcal/mol, which can be classified as a strong N–H acid. This significant increase in acidity is mainly due to the expansion of the π-conjugate system, which stabilizes the corresponding anion and thus improves its acidity. Also, the NICS index of the five-membered ring has drastically increased (−10.85 ppm) as well as the HOMA index (0.83), which indicates the importance of this ring in stabilizing the negative charge in the anion **(14-H)**$^-$.

In addition, the effects of four cyano groups on the acidity of compound **14** were also investigated. The remarkable stability of compound **17** with $\Delta H_{acid} = 276.3$ kcal/mol indicated that this compound is the strongest superacid among the examined structures. Among the studied hybrid organic–inorganic acids **18–23**, it can be clearly observed that the acidity of the compounds based on sulfuric acids **18–20** has remarkably increased and the strongest superacids have been obtained with acidity in the range of 285.4–291.9 kcal/mol. All the proposed acids **18–20** are more acidic than $H_2SO_4$ ($\Delta H_{acid} = 311.5$ kcal/mol) and $FSO_3H$ ($\Delta H_{acid} = 301.3$ kcal/mol) [37]. Superacid **20** based on trifluoromethane sulfonic acid (trifilic acid) meets the high acidity 285.4 kcal/mol. This can be attributed to the electron-withdrawing group of $-CF_3$, which has well improved the stability of the negative charge in the conjugate base. It is also observed that adding of fluorine atom instead of the hydroxyl group in the sulfuric acid-based superacid **18** (compound **19**) has led to a slight increase in the acidity compared to compound **18** by about 5.5 kcal/mol. Figure 5 shows a comparison between the bond lengths in **19** and its corresponding conjugate base **(19-H)**$^-$. As would be observed, due to the negative charge stability in the conjugate base of **19**, the bond lengths have increased in the five-membered ring, which indicates the presence of resonance phenomena in anion structure **(19-H)**$^-$.

Finally, it was claimed that for the conjugate bases of **1–23**, the negative charge is placed on the cyclopentadiene ring. Molecular electrostatic potential (MEP) maps can also be used to support this claim [38]. The MEP map provides the charge distributions of molecules in three-dimensional space, the positive (blue) and negative (red). Calculated acidities at B3LYP/6–31 + + G(d,p) level are the highest for molecules **17** and **20**. Therefore as representative examples, MEP maps of **17** and **20** and the corresponding conjugate bases are shown in Fig. 6. As would be observed, the negative charge in **(17-H)**$^-$ and **(20-H)**$^-$ is placed on the five-membered ring. Some common features can be observed in the MEP maps. The positive charge (blue region) is mainly localized on the hydrogen atom of the acid unit, and this will favor deprotonation. The regions governing the electron-rich nitrile groups in **(17-H)**$^-$ are strongly negative (red color), which confirms the

**Fig. 4** Strong intramolecular hydrogen bonding in the structures of **2** and **6**



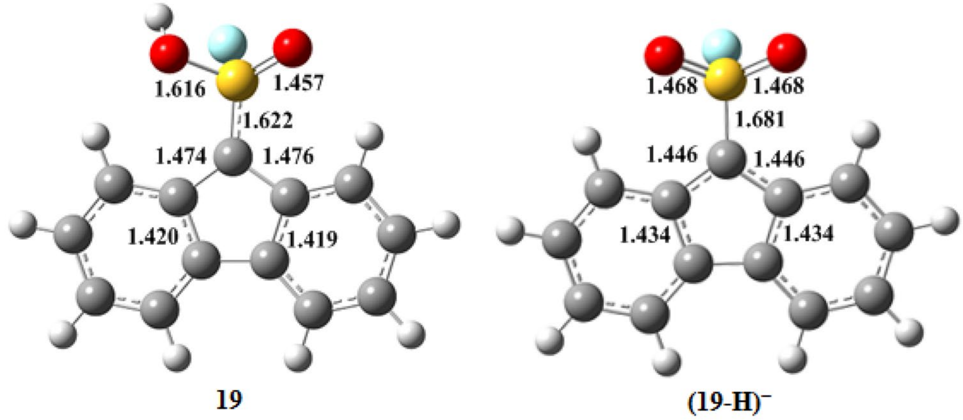



**Fig. 5** The optimized structures of **19** and **(19-H)**$^{-}$. The bond distances are in (Å)

high capacity of –CN group for delocalization of negative charge. It can be seen from MEP of **(20-H)**$^{-}$ that the negative charge is distributed throughout the structure.

Finally, to examine the acidity of the designed molecules in solution phase, the theoretical studies on 9H-fluorene, **1**, **14**, and **19** in dimethylsulfoxide (DMSO) were

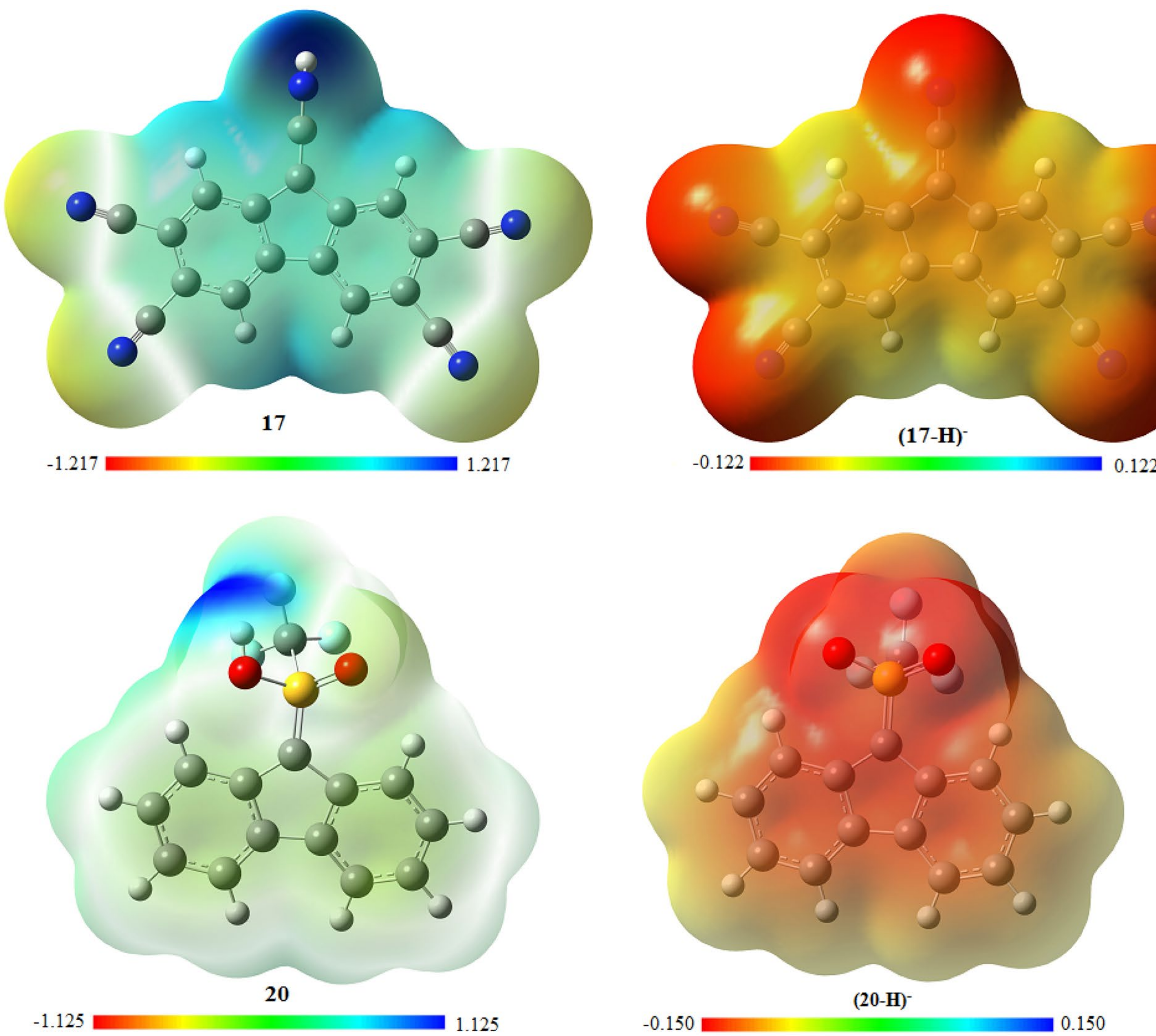



**Fig. 6** Molecular electrostatic potential surface for acid **17** and **20,** as well as their conjugate bases

**Table 4** The calculated $\Delta_r H_{DMSO}$ and $pK_a$ (theor), for 9H-fluorene, **1**, **14**, and **19** in DMSO as solvent

| Parameter | Molecule | | | |
|---|---|---|---|---|
| | **Fluorene** | **1** | **14** | **19** |
| $\Delta_r H_{DMSO}$[a] | 48.4 | 22.3 | 12.8 | −11.8 |
| $pK_a$ (theor) | 24.3 | 7.0 | 0.7 | −15.5 |

[a]B3LYP/6–31++G(d,p), kcal/mol, at 298 K

performed using the conductor-like polarizable continuum model (CPCM), through DFT calculations done at B3LYP/6–31++G(d,p) method. It should be mentioned that the CPCM model is often considered one of the most successful solvation models [39]. The proton transfer reaction between the proposed acids and DMSO molecules can be considered to estimate acidities in DMSO. The protonation enthalpies of DMSO by the acids in solution ($\Delta_r H_{DMSO}$) were calculated according to the Eq. (5):

$$AH + DMSO \rightarrow A^- + DMSOH^+ + \Delta_r H_{DMSO} \quad (5)$$

The $pK_a$s of the studied acids in DMSO were calculated using the $\Delta_r H_{DMSO}$ values and the empirical Eq. (6) [40–42]:

$$pK_a(\text{theor}) = 0.661 \times \Delta_r H_{DMSO} - 7.7 \quad (6)$$

The calculated $\Delta_r H_{DMSO}$ and $pK_a$ (theor) values of 9H-fluorene, **1**, **14**, and **19** in DMSO are collected in Table 4.

It should be mentioned that calculated $\Delta_r H_{DMSO}$ values are in good agreement with the experimental $pK_a$ values for a wide variety of organic acids with the average absolute error of 1.1 in $pK_a$ unit [40–42]. As shown in Table 4, the calculated $pK_a$ (theor) value for 9H-fluorene at B3LYP/6–31+G(d,p) level of theory is 24.3 which is close to the experimental value ($pK_a$ = 22.6 in DMSO) [24]. The data in Table 4 show that the molecule **14** is a moderate acid, while the calculated $pK_a$ of the acid **19** indicates its superacidity in DMSO solvent.

## Conclusion

A new category of organic fluorene acids (23 structures) was designed, and their acidities were investigated by DFT/B3LYP/6-31++G(d,p) method. Some designed structures are more acidic than fluorene and even inorganic acids such as $H_2SO_4$ and $FSO_3H$. Upon deprotonation, the negative charge is delocalized in the cyclic framework, which led to an aromatic system. This is in harmony with aromatic indices (NICS and HOMA) and MEP analysis of the corresponding conjugate base of acids. Substitution of electron-withdrawing groups, –CN and –F, on cyclic framework enhanced the acidity. The $\Delta H_{acid}$ values were calculated in the range of 276.2–328.2 kcal/mol, which some fall into the defined range of superacidity. The proposed acids are not prepared as yet. They can be used in the organic syntheses as strong acid and catalysts, and their synthesis is strongly recommended.

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**Availability of data and material** The online version of this article contains supplementary material, which is available to authorized users.

## Declarations

**Conflict of interest** The authors declare no competing interests.

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