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# Fluorine–Substituted Phenols as Probes to Study Intermolecular Proton Transfer Induced by Excess Electron Attachment to Uracil–Phenol Complexes

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# Fluorine–Substituted Phenols as Probes to Study Intermolecular Proton Transfer Induced by Excess Electron Attachment to Uracil–Phenol Complexes[#]

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**Abstract**

**Motivation.** The experiments suggest that low–energy electrons, possibly localized on nucleic acid bases, induce DNA damage. The results of our recent studies strongly suggest that the excess electron attachment to the complex of a nucleic acid base with an amino acid can induce a barrier–free proton transfer (BFPT) from the amino acid to the O8 of uracil. The driving force for the proton transfer is to stabilize the excess electron localized on a π* orbital. Our further studies also demonstrated that BFPT occurs in anionic complexes of uracil with alanine, formic acid, as well as $H_2Se$ and $H_2S$. We briefly determined factors governing the occurrence of proton transfer in complexes between anionic nucleic acid bases (NABs) and proton donors. We found that the occurrence of BFPT in the uracil complexes is an outcome of the interplay between the deprotonation energy of a proton donor and the protonation energy of the anion of uracil.

**Method.** The density functional theory (DFT) was applied as our research method. The B3LYP and MPW1K exchange–correlation functionals with 6–31++G** (5d) basis set were used.

**Results.** The substitution of five hydrogen atoms with fluorine atoms in phenol molecule decreases the energy of deprotonation from 15.3 eV to 14.4 eV. There are 5 groups of F–substituted phenol isomers and 19 structures in total. These 19 molecules provide fine grid on the scale of deprotonation energy and can be used as a probe to study the BFPT phenomenon. In the case of uracil–2,3,4,5,6–pentafluorophenol and uracil–2,4,6–trifluorophenol complexes, the excess electron attachment can induce BFPT from the hydroxyl group to the O8 atom of U, with the products being a hydrogenated uracil and a deprotonated fluorophenol. No BFPT is predicted for the anions of other uracil–phenol complexes.

**Conclusions.** The estimated critical value of deprotonation energy of a F–substituted phenol for which BFPT takes place is 14.86–15.38 eV. Further studies can be preformed to obtain a higher accuracy of this estimation.

**Keywords.** Barrier–free proton transfer; uracil; DNA damage by low energy electrons.

**Abbreviations and notations**

| | |
|---|---|
| BFPT, barrier–free proton transfer | NAB, nucleic acid base |
| $E_{DP}$, deprotonation energy | PD, proton donor |
| $G_{DP}$, deprotonation Gibbs free energy | PT, proton transfer |
| $H_{DP}$, deprotonation enthalpy | VDE, vertical detachment energy |

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# 1 INTRODUCTION

Low–energy electrons are produced in large quantities by high–energy radiation interacting with condensed phases [1]. The recent experiments of Sanche *et al*. [1] suggest that low–energy electrons (with energies well below the ionization potential of nucleic bases) can induce DNA damage. However, in contrast to the reactions between genetic material and reactive compounds such as $HO^{\bullet}$ radicals, alkylating and oxidizing agents, and halogens, low–energy electrons trigger single– and double–strand breaks in DNA.

Electron trapping on nucleic acid bases has been an important topic in radiation biology for several decades. About ten years ago, it was realized that the large polarities of NABs allow for the existence of dipole–bound anionic states [2]. While our recent CCSD(T) results indicate that the valence anionic state of uracil (U) is vertically stable with respect to the neutral by 0.507 eV, [3] our calculations also find the valence anonic state to be thermodynamically unstable by 0.215 eV with respect to the dipole–bound anionic state and by 0.147 eV with respect to the neutral [3]. The current view is that valence anionic states are unbound, or at best very weakly bound, for isolated NABs, but that they become dominant for solvated species [4].

Intra– and intermolecular tautomerizations involving nucleic acid bases have long been suggested as critical steps in mutations of DNA [5–7]. Intramolecular proton transfer reactions have been studied for gas–phase and hydrated nucleic acid bases [7–11]. The single and double proton transfers have been studied for ground and excited electronic states of pairs of NABs [12–17]. The proton transfer reactions in the GC system have been found favorable for anions and unfavorable for the cation [17]. Small kinetic barriers were reported for the last reaction.

The results of our studies on complexes of a model NAB, uracil, with glycine suggest that valence–type anions of nucleic bases possess centers with high proton affinities, as a result of which a proton can be transferred to the anionic base. Moreover we recently reported the discovery of a tautomerization process that occurs in the uracil–glycine complex upon excess electron attachment [3]:

$$U\ldots HA + e^{-} \rightarrow UH^{\bullet}\ldots A^{-} \qquad (1)$$

Our *ab initio* calculations and photoelectron spectroscopic measurements (PES) from the group of Kit Bowen strongly suggested that the electron attachment to complexes of uracil with glycine leads to a barrier–free proton transfer (BFPT) from the acid (HA) to the O8 atom of U with the products being a neutral radical of hydrogenated uracil ($UH^{\cdot}$) and an anion of the deprotonated amino acid [3]. A driving force for the proton transfer is to stabilize the excess electron on a $\pi^*$ orbital of the anionic base (see Fig. 1 for the numbering of atoms in uracil and the excess electron orbital in its valence $\pi^*$ anionic state).

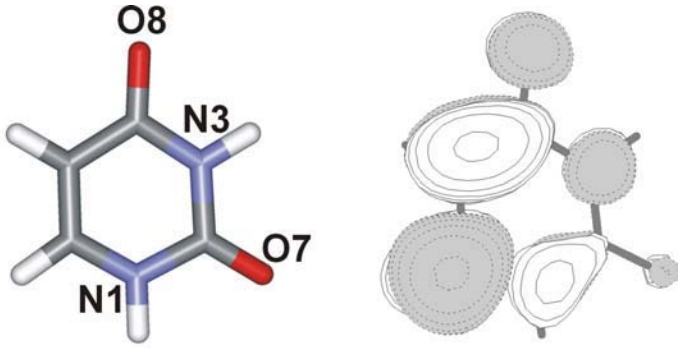


**Figure 1.** Uracil and single occupied molecular orbital π*.

Our further studies also demonstrated that BFPT occurs in anionic complexes of uracil with alanine [18], formic acid [19] as well as $H_2Se$ and $H_2S$ [20]. We briefly determined factors governing the occurrence of proton transfer in complexes between an anionic NAB and a proton donor. We found that the occurrence of BFPT is an outcome of the interplay between the deprotonation energy of a proton donor and the protonation energy of the anion of uracil. For example, we found that the deprotonation energy of water ($E_{DP}$ = 17.16 eV, $H_{DP}$ = 16.86 eV) is too high to facile BFPT [20], but the deprotonation energy of $H_2Se$ ($E_{DP}$ = 14.95 eV, $H_{DP}$ = 14.78 eV) is sufficiently small to allow proton transfer to the anion of uracil [20].

We also found that the stabilization energy of a complex ($E_{stab}$) has the influence on the occurrence of BFPT, and we analyzed critical hydrogen bonds that develop in anionic complexes. For example, in the case of anionic $UH_2A$ complexes (A = O, S, Se), we reported that the increased stabilities of anionic complexes that undergo BFPT can be related to the properties of the second hydrogen bond (C5H…$A^-$, N1H…$A^-$ or N3H…$A^-$). In comparison with the neutral structures, this bond is weakened for anionic structures without BFPT and strengthened for those with BFPT [20].

BFPT (or proton transfer (PT) with a low kinetic barrier (LBPT)) may also take place in DNA. To elucidate the fate of primary anionic states generated in DNA irradiated with low–energy electrons one needs, therefore, to determine, in detail, factors governing the occurrence of PT in complexes between anionic nucleic bases and a proton donor (PD).

In this paper we present an approach that may help to find the critical value of the deprotonation energy of a proton donor for which BFPT occurs for a given NAB. We propose here to use fluoro–substituted phenols as probes. The deprotonation energy changes from 15.375 eV for unmodified phenol to 14.384 eV for penta–fluoro–substitued 2,3,4,5,6–pentafluorophenol. The energy range of 15.38–14.38 eV is exactly in the region, which is important for BFPT in anionic complexes of uracil with PDs.

Our first results show that in the case of the 2,3,4,5,6–pentafluorophenol–uracil and 2,4,6–trifluorophenol–uracil complexes, the excess electron attachment induces BFPT from the hydroxyl group of $C_5F_6OH$ or $C_5H_2F_3OH$ to the O8 atom of U, with the products being a hydrogenated uracil

and a deprotonated F–substituted phenol. No BFPT is predicted for the anions of other uracil–phenol complexes.

## 2 MATERIALS AND METHODS

The notation PnFxyz will be used for the phenol and fluorine–substituted phenol molecules. The symbol n indicated how many fluorine atoms are in the molecule and the symbols x, y, z etc. indicate positions of the fluorine atoms in the phenol ring. The examples of this notation are presented in Table 1. In the case of anionic complexes we will use a notation aPnFxyz$U_s$ where n, x, y and z are defined as above and s designates the side of the O8 atom of uracil to which the phenol is coordinated. Figures 2–5 provide examples of this notation.

The stability of anionic complexes is expressed in term of Estab. Estab is defined as a difference in electronic energies of the monomers and the dimer. The values of Estab were not corrected for basis set superposition errors because our earlier results demonstrated that the values of this error in the B3LYP/6–31++G** calculations for a similar neutral uracil–glycine complex did not exceed 0.06 eV.

As our research method we applied density functional theory (DFT) [21–22] with a Becke's three–parameter hybrid functional (B3LYP) [23–25] and a modified Perdew–Wang 1–parameter–method for kinetics (MPW1K) designed by Truhlar *et al*. [26]. In both DFT approaches we used the same 6–31++G** basis set [27–28]. Five d functions were used on heavy atoms. The calculations of matrices of second derivatives of energy (Hessians) were performed to confirm that final geometries were minima on potential energy surfaces.

The usefulness of the B3LYP/6–31++G** method to describe intra– and intermolecular hydrogen bonds has been demonstrated in recent studies through comparison with the second order Møller–Plesset (MP2) predictions [29–32]. The ability of the B3LYP method to predict excess electron binding energies has recently been reviewed and the results were found to be satisfactory for valence–type molecular anions [33]. We found that the value of vertical detachment energy (VDE) determined at the B3LYP/6–31++G** level for the valence $\pi^*$ anionic state of an isolated uracil is overestimated by 0.2 eV in comparison with the CCSD(T)/aug–cc–pVDZ result [2]. We will assume in the following that the same correction of 0.2 eV applies to the values of VDE for all anionic aPnFxyz$U_s$ complexes in which an excess electron occupies a $\pi^*$ orbital localized on uracil.

It is known that the B3LYP method underestimates barriers for proton transfer reactions [26], and thus, lack of a barrier for a proton transfer reaction may be an artifact of the B3LYP method. For this reason, we performed additional geometry optimizations using a hybrid exchange–correlation potential MPW1K, which was parameterized to reproduce barrier heights for chemical

reactions [26,34]. The MPW1K functional was optimized against a database of 40 barrier heights and 20 energies of reaction [26,34]. The performance of this functional for geometries of saddle points and barrier heights was found to be superior to that of the B3LYP functional as well as the second order Møller– Plesset method [26].

All calculations were carried out with the GAUSSIAN 98 code [35] on a cluster of Intel/Xeon and Intel/Pentium3 nodes and on the IBM SP/2 supercomputer (NERSC).

# 3 RESULTS AND DISCUSSION

## 3.1 The Probe

A series of fluoro–substituted phenols (PnFxyz) has been designed with the $H_{DP}$ in a range of 14.07–15.05 eV (see Table 1). The fluoro–substitution of phenol gives 5 groups of isomers (including unmodified phenol) and 19 molecules in total. The most basic molecule considered by us is the standard phenol ($E_{DP}$ = 15.38 eV; $H_{DP}$ = 15.05 eV) and the most acidic is $C_6F_5OH$ (2,3,4,5,6–pentafluorophenol), with $H_{DP}$ = 14.07 eV ($E_{DP}$ = 14.38 eV). The resulting grid for $H_{DP}$ values is dense, with the neighboring values separated by less than 0.143 eV.

The enthalpies and free energies of deprotonation are systematically overestimated at the B3LYP/6–31++G** (5d) electronic structure level. The discrepancies between the calculated and measured values of $H_{DP}$ are contained in a range of 0.138–0.368 eV.

**Table 1.** The calculated B3LYP/6–31++G** (5d) and measured values of $E_{DP}$, $H_{DP}$ and $G_{DP}$ of the series of fluoro–substituted phenols. All values in eV.

| Symbol | F–substituted phenol | $E_{DP}$ | $H_{DP}$ | $G_{DP}$ | $H_{DP}^{exp}$ | $G_{DP}^{exp}$ |
|---|---|---|---|---|---|---|
| P0F | Phenol | 15.375 | 15.045 | 14.702 | 15.190±0.026 [a] | 14.837±0.087 [b] |
| P1F2 | *o*–Fluorophenol | 15.117 | 14.791 | 14.444 | 14.971±0.095 [b] | 14.691±0.087 [b] |
| P1F3 | *m*–Fluorophenol | 15.103 | 14.781 | 14.436 | 14.899±0.091 [b] | 14.598±0.087 [b] |
| P1F4 | *p*–Fluorophenol | 15.231 | 14.910 | 14.566 | 15.033±0.092 [b] | 14.733±0.087 [b] |
| P2F23 | 2,3–Difluorophenol | 14.869 | 14.550 | 14.204 | | |
| P2F24 | 2,4–Difluorophenol | 14.978 | 14.662 | 14.317 | | |
| P2F25 | 2,5–Difluorophenol | 14.838 | 14.519 | 14.173 | | |
| P2F26 | 2,6–Difluorophenol | 14.997 | 14.669 | 14.317 | | |
| P2F34 | 3,4–Difluorophenol | 14.975 | 14.657 | 14.309 | | |
| P2F35 | 3,5–Difluorophenol | 14.842 | 14.523 | 14.176 | | |
| P3F234 | 2,3,4–Trifluorophenol | 14.743 | 14.428 | 14.080 | | |
| P3F235 | 2,3,5–Trifluorophenol | 14.602 | 14.287 | 13.940 | | |
| P3F236 | 2,3,6–Trifluorophenol | 14.745 | 14.424 | 14.072 | | |
| P3F245 | 2,4,5–Trifluorophenol | 14.715 | 14.401 | 14.053 | | |
| P3F246 | 2,4,6–Trifluorophenol | 14.860 | 14.543 | 14.191 | | |
| P4F2356 | 2,3,5,6–Tetrafluorophenol | 14.493 | 14.178 | 13.824 | 14.546±0.124 [c] | |
| P4F2456 | 2,4,5,6–Tetrafluorophenol | 14.619 | 14.305 | 13.950 | | |
| P4F3456 | 3,4,5,6–Tetrafluorophenol | 14.493 | 14.180 | 13.827 | | |
| P5F | 2,3,4,5,6–Pentafluorophenol | 14.384 | 14.073 | 13.712 | 14.215±0.095 [d] | 13.904±0.087 [d] |

[a–d] Ref [35]

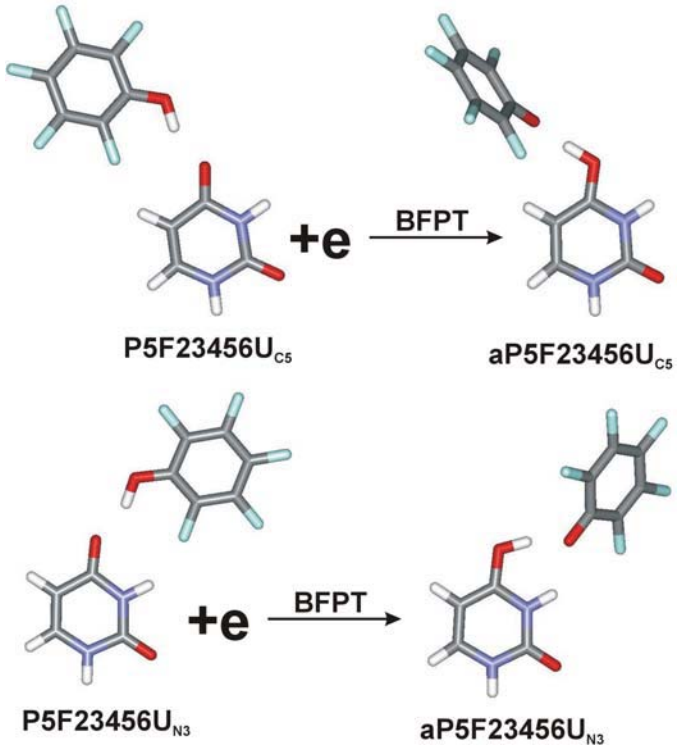


**Figure 2.** The excess electron attachment induces barrier free proton transfer in the U…$HOC_6F_5$ complexes.

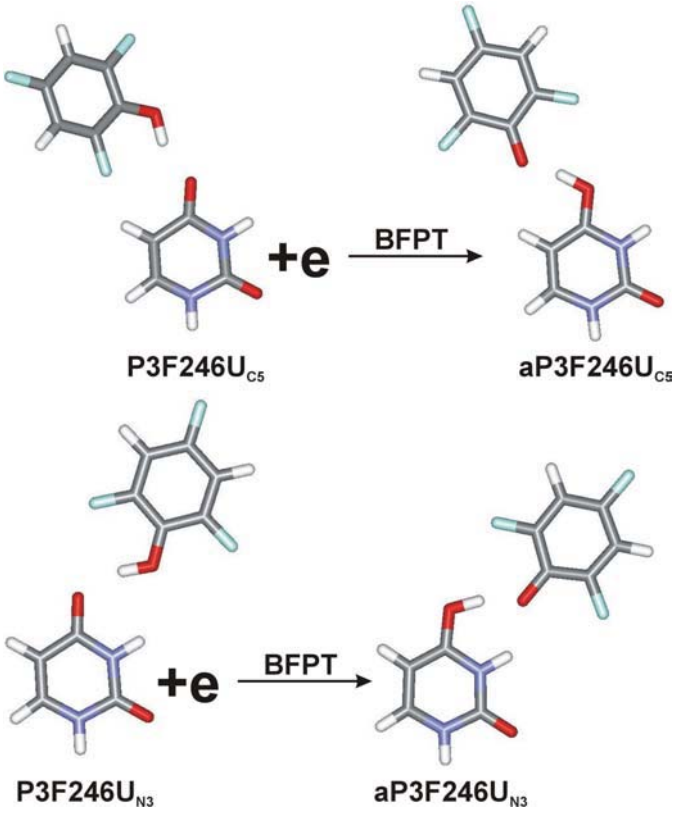


**Figure 3.** The excess electron attachment induces barrier free proton transfer in the U…$HOC_6H_2F3$ complexes.

## 3.2 The Complex

Earlier results on anionic complexes of uracil with amino acids [3] and carboxylic acids [19] indicate that the most stable structures are obtained when a proton donor molecule is bound to the uracil's O8 atom. A preference to form a hydrogen bond with O8 rather than with O7 is dictated by the fact that the excess π* electron is localized in the neighborhood of the O8 atom and hydrogen bonding on the O8 site stabilizes the anionic state. These earlier findings prompted us to restrict the topological space of the aPnFxyzU$_s$ complexes to structures with a hydrogen bond between the hydroxyl group of an F–substituted phenol and O8 of uracil. In these structures, the hydroxyl group has a dual role acting as both a proton donor and a proton acceptor.

Two such structures are possible with the proton donor site of uracil being either the N3H or C5H group (see Figures 1–4) and the resulting complex between the PnFxyz phenol and uracil will be labeled PnFxyzU$_{C5}$ and PnFxyzU$_{N3}$, respectively. The PnFxyzU$_{C5}$ and PnFxyzU$_{N3}$ structures are analogous to the UG14 and UG16 structures, respectively, for the uracil–glycine complexes [29]. The anionic UG14 and UG16 structures were the two most stable among those in which an OH group acts as both a proton donor and a proton acceptor.

The anionic aPnFxyzUs complexes are shown in Figures 2–4. A common feature of anionic wave functions identified by us for the aPnFxyzUs complexes is that the excess electron is localized on a π* orbital of uracil, in close resemblance to the valance anionic state of isolated uracil (see Figures 1 and 5).

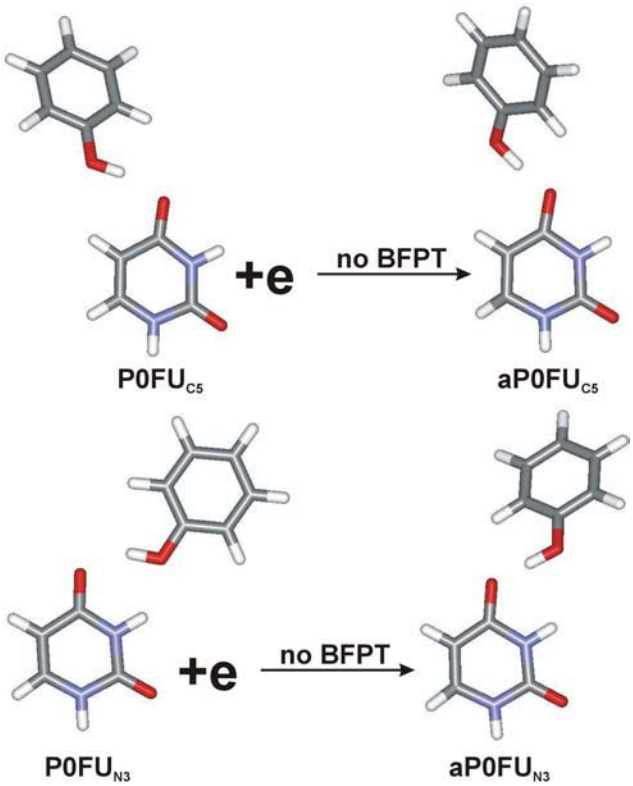


**Figure 4.** The excess electron attachment does not induce barrier free proton transfer in the U…HOC$_6$H$_5$ complexes.

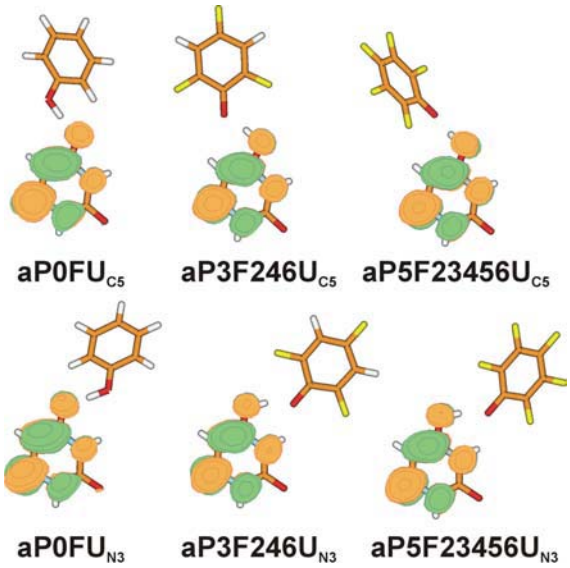


**Figure 5.** The excess electron occupies a π* orbital in all investigated anionic complexes.

Our most important finding is that the most stable anionic complexes of U with P3F246 and P5F23456 are characterized by BFPT from the F–substituted phenol to the O8 atom of uracil; see Table 2 and Figure 2 and 3. A driving force for the proton transfer is to stabilize the excess negative charge, which is primarily localized in the O8–C4–C5–C6 region (see Figure 5). In consequence of the extra stabilization of the excess electron provided by the transferred proton, the value of VDE for the anionic aP3F246U and aP5F23456U complexes are larger by 1.5–1.8 eV than those for the valance anion of an isolated uracil. In fact, the B3LYP/6–31++G** values of VDE for these structures span a range of 2.16–2.23 eV for aP3F246U and 2.38–2.50 eV for aP5F23456U, respectively (1.96–2.03 and 2.18–2.30 eV, respectively, after the CCSD(T) correction).

**Table 2.** The B3LYP/6–31++G** (5d) energy stabilization of anionic complexes together with vertical detachment energy (VDE).

| Complex | Energy [eV] | | BFPT (yes/no) | |
|---|---|---|---|---|
| | $E_{stab}$ | VDE | B3LYP | MPW1K |
| aP0FU$_{C5}$ | 1.007 | 1.473 | No | No |
| aP0FU$_{N3}$ | 0.976 | 1.444 | No | No |
| aP3F246U$_{C5}$ | 1.153 | 2.231 | Yes | Yes |
| aP3F246U$_{N3}$ | 1.202 | 2.156 | Yes | Yes |
| aP5F23456U$_{C5}$ | 1.449 | 2.503 | Yes | Yes |
| aP5F23456U$_{N3}$ | 1.511 | 2.379 | Yes | Yes |

We performed additional MPW1K/6–31++G** geometry optimizations for all anionic complexes considered in this study to validate the B3LYP predictions as to the occurrence of intermolecular proton transfer. The B3LYP and MPW1K predictions are qualitatively consistent (Yes/No in Table 2).

For phenol (aP0FU), both exchange–correlation functionals predict that anionic complexes with U can be viewed as U– solvated by phenol and BFPT does not occur (see Figure 4). The calculated

values of VDEs for these structures are in a range 1.44–1.47 eV (1.24–1.27 eV after the CCSD(T) correction).

## 4 CONCLUSIONS

A series of fluoro–substituted phenols (PnFxyz) can be designed with the $H_{DP}$ values in a range of 14.07–15.05 eV. The fluoro–substitution of phenol gives 5 groups of isomers and 19 molecules in total. The most basic molecule considered by us is the standard phenol ($H_{DP}$ = 15.05 eV) and the most acidic is 2,3,4,5,6–pentafluorophenol, with $H_{DP}$ = 14.07 eV. The deprotonation enthalpies of 19 molecules provide a fine grid on the scale of $H_{DP}$.

The fluorine–substituted phenols can be used as probes designed to study proton transfer reactions. Either theoretical or experimental studies on complexes of different F–substituted phenols can provide the estimation of the critical value of deprotonation enthalpy (or $E_{DP}$ or $G_{DP}$) for which the intermolecular PT reaction occurs for a given NAB.

The results of density functional calculations with the B3LYP and MPW1K exchange–correlation functionals indicate that an excess electron in the aPnFxyzU complexes is described by a $\pi^*$ orbital localized on the ring of uracil. In the case of the P3F246U and P5F23456U complexes, the excess electron can induce BFPT from the F–substituted phenol to the O8 atom of uracil. The driving force for the proton transfer is to stabilized the negative excess charge localized primarily on the O8–C4–C5–C6 fragment of uracil. The barrier–free nature of the proton transfer process has been confirmed using the MPW1K functional. For aP5F23456U the estimated values of VDE are in a range 2.4–2.5 eV (2.2–2.3 eV after the CCSD(T) correction). The estimated values of VDE for aP3F246U, which also undergoes BFPT, are about 2.2 eV (2.0 eV after the CCSD(T) correction).

For anionic complexes of uracil with phenol (aP0FU), both exchange–correlation functionals predict that the structure has the character of U– solvated by phenol and BFPT does not occur. The estimated VDE for these structures are in a range 1.4–1.5 eV (1.2–1.3 eV after the CCSD(T) correction).

To summarize, our study on the effects of excess electron attachment to the complexes of uracil with F–substituted phenols suggest that critical value of $E_{DP}$ for which BFPT occurs is in a range of 14.7–15.3 eV. Further studies on anionic complexes of uracil with mono, di and tri substituted phenols can be performed to obtain a more precise value of $E_{DP}$ for which BFPT occurs.

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