

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 H₂Se and H₂S. 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 performed 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	PD, proton donor
E _{DP} , deprotonation energy	PT, proton transfer
G _{DP} , deprotonation Gibbs free energy	VDE, vertical detachment energy
H _{DP} , deprotonation enthalpy	
NAB, nucleic acid base	

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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[•] 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 NAB's 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 anionic 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 NAB's, 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 NAB's.[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 tautomerisation process that occurs in the uracil-glycine complex upon excess electron attachment:[3]



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[•]) and an anion of the deprotonated amino acid.[3] A driving force for the proton transfer is to stabilize the excess electron on a π^* orbital of the anionic base (see Fig. 1 for the numbering of atoms in uracil and the excess electron orbital in its valence π^* anionic state).

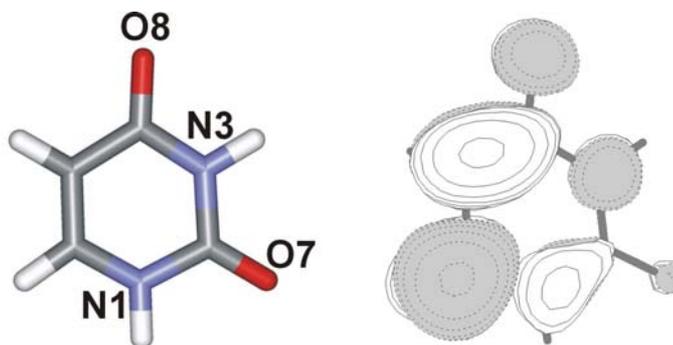


Figure 1. Uracil and single occupied molecular orbital π^* .

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 anionic NAB's and proton donors. 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 ($E_{\text{DP}}=17.16$ eV, $H_{\text{DP}}=16.86$ eV) is too high to facilitate BFPT,[20] but the deprotonation energy of H_2Se ($E_{\text{DP}}=14.95$ eV, $H_{\text{DP}}=14.78$ 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 ($\text{A}=\text{O}, \text{S}, \text{Se}$), we reported that the increased stabilities of anionic complexes that undergo BFPT can be related to the properties of the second hydrogen bond ($\text{C5H}\dots\text{A}^-$, $\text{N1H}\dots\text{A}^-$ or $\text{N3H}\dots\text{A}^-$). 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-substituted 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 $\text{C}_5\text{F}_6\text{OH}$ or $\text{C}_5\text{H}_2\text{F}_3\text{OH}$ 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 aPnFxyzU_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 π^* 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 aPnFxyzU_s complexes in which an excess electron occupies a π^* 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 C₆F₅OH (2,3,4,5,6-pentafluorophenol), with H_{DP} =14.07 eV (E_{DP} =14.38 eV). The resulting grid of H_{DP} 's 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.

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] (a-d)

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.

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 Figs. 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.

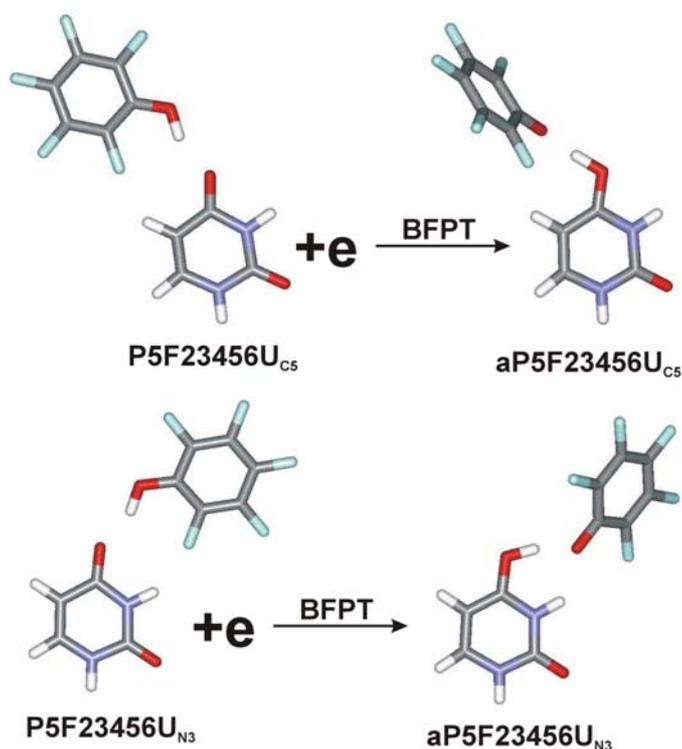


Figure 2. The excess electron attachment induces barrier free proton transfer in the U...HOC₆F₅ complexes.

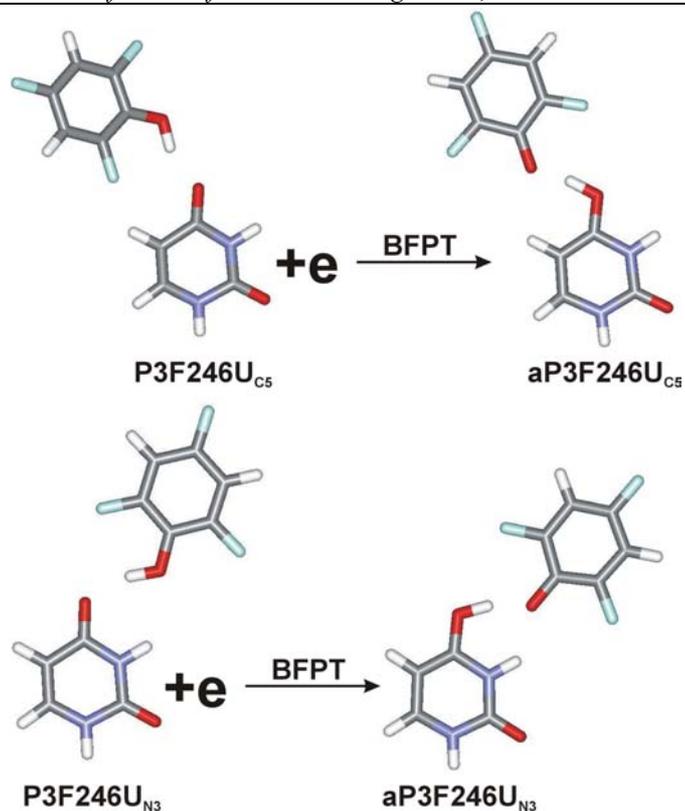


Figure 3. The excess electron attachment induces barrier free proton transfer in the $U\dots HOC_6H_2F_3$ complexes.

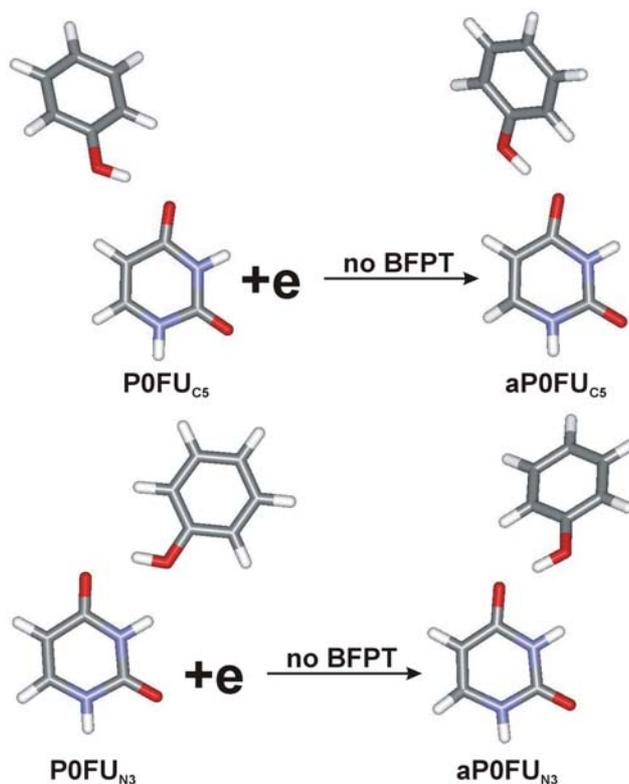


Figure 4. The excess electron attachment does not induce barrier free proton transfer in the $U\dots HOC_6H_5$ complexes.

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 valence anionic state of isolated uracil (see Figs. 1 and 5).

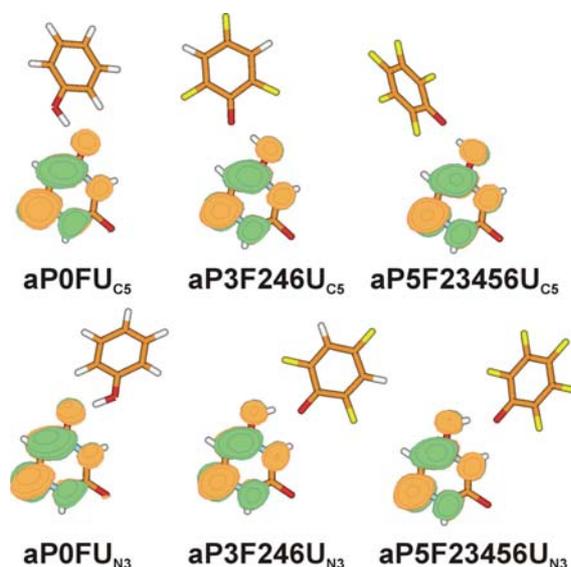


Figure 5. The excess electron occupies a π^* orbital in all investigated anionic complexes.

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 valence 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).

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

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

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 π^* 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 stabilize 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 EDP 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 EDP for which BFPT occurs.

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Biographies

Maciej Haranczyk has graduated with M.Sc. degree in Chemistry at the University of Gdansk. He is about to start PhD studies. Maciej Haranczyk has worked on proton transfer in radical systems for last 3 years and he has collaborated with Dr. Janusz Rak (University of Gdansk, Poland) and Dr. Paul J.A. Ruttink (University of Utrecht, Holland).

Maciej Gutowski is a computational chemist at the Pacific Northwest National Laboratory. After obtaining a Ph.D. degree in theoretical chemistry from the University of Warsaw under supervision of Prof. L. Piela, he undertook postdoctoral research with Prof. J. Simons at the University of Utah. Maciej's research interests cover electronic structure of molecules, surfaces, and solids and his ongoing projects are on: (i) atomic and electronic structure of damaged DNA, (ii) epitaxial interfaces of type II heterojunctions, and (iii) materials for hydrogen storage.
