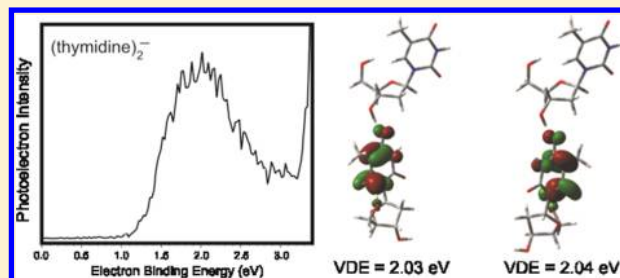


Photoelectron Spectroscopy and Computational Modeling of Thymidine Homodimer Anions

Piotr Storoniak,[†] Janusz Rak,^{*,†} Yeon Jae Ko,[‡] Haopeng Wang,[‡] and Kit H. Bowen^{*,‡}[†]Department of Chemistry, University of Gdańsk, Sobieskiego 18, 80-952 Gdańsk, Poland[‡]Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, United States

S Supporting Information

ABSTRACT: The intact thymidine homodimer anion (dT_2^-) was generated in the gas phase using an infrared desorption/photoemission source and recorded by a pulsed photoelectron spectrometer. The photoelectron spectrum (PES) revealed a broad signal with the maximum at electron binding energy ~ 2.0 eV and the threshold value at 1.1 eV. The relative energies and vertical detachment energies of the possible anion structures were calculated at the B3LYP/6-31++G(d,p) level. Here we report that the most stable anion radical homodimer geometries observed in the PES are the anionic nucleoside coordinated by the O8 atom of thymine to the deoxyribose of the second neutral nucleoside. Unlike previous experimental–computational studies on anionic complexes involving nucleobases with proton donors, the electron-induced proton-transferred structures are not responsible for the shape of the PES of dT_2^- .



■ INTRODUCTION

Numerous experimental^{1,2} and theoretical^{3–11} investigations on electron interactions with nucleobases have demonstrated that gas phase anionic nucleobases, i.e., in isolation, support adiabatically stable dipole bound anions, while their valence anions are unbound or weakly bound. However, the valence anions of isolated nucleobases may be stabilized provided that additional inter- or intramolecular interactions are present. This has been clearly shown in photoelectron spectroscopy (PES)^{12–14} and Rydberg electron transfer (RET) techniques¹⁵ by solvating nucleobases with noble gas atoms or water molecules. Our previous studies combining gas phase PES experiments with theoretical calculations have shown that the valence nucleobase anions formed were significantly stabilized when solvated by various proton donors, which include the following: anionic hydrogen-bonded complexes of nucleobases with amino acids,^{16,17} inorganic acids,¹⁸ formic acid,^{19,20} and alcohols.²¹ We had also discovered that the above systems may be additionally stabilized by intermolecular proton transfer (PT) upon electron attachment.

Such a comprehensive PES/computational approach has also been applied to dimers of complementary nucleobases.^{22–24} This resulted in the identification of the most stabilizing hydrogen-bonding pattern within the anionic radical dimers of guanine–cytosine (GC^-), adenine–thymine (AT^-), and their N-methylated derivatives (9MG-1MC^- and 9MA-1MT^-). Our studies, consistent with earlier theoretical reports on AT^- and GC^- ,^{25–31} indicated that the presence of a purine significantly increases the stability of the pyrimidine valence anions. Analogous to the aforementioned nucleobase complexes, PT also appears to be of great importance, especially for

the GC^- and the nucleoside pair of dG-dC^- ,^{25–27,32–34} and in particular, homodimer anions of nucleobases U_2^- , T_2^- , C_2^- , A_2^- , and G_2^- .³⁵ In addition to intermolecular PT, an intramolecular PT induced by electron attachment was demonstrated by Kobylecka et al. in their computational study on 2'-deoxyadenosine-5'-monophosphate ($\text{S}'\text{-dAMPH}$).³⁶ This computational result reproduced the photoelectron spectrum of $\text{S}'\text{-dAMPH}^-$, thus confirming the occurrence of intramolecular PT within a stable valence anion of studied nucleotides in the gas phase.³⁷ As far as the valence anions of nucleosides are concerned, Bowen et al. measured the photoelectron spectra of three 2'-deoxyribonucleoside (dT^- , dC^- , dA^-) and four ribonucleoside (rU^- , rC^- , rA^- , rG^-) anions confirming that nucleosides can exist as stable valence anions in the gas phase.³⁸

The present report is a continuation of our previous PES studies on single nucleosides³⁸ and homodimers of nucleic acid bases.³⁵ In this current experimental–computational effort, the PES for the thymidine homodimer anion (dT_2^-) was recorded in the gas phase. The extension of this system beyond the thymine homodimer anion (T_2^-) and single thymidine nucleoside anion (dT^-) afforded estimation of the effects of base–base and sugar–base hydrogen bonding on electron-capturing ability. Interpretation of our measured PES feature at an electron-binding energy of ~ 2 eV involved theoretical studies considering possible arrangements of the complex. Past PES and computational studies^{17,20,24,35} revealed that the most

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stable gas phase anions originate from electron-induced barrier-free PT to the O8 atom of thymine and are characterized by a VDE around 2 eV. However, our calculations show that the most likely anionic homodimer arrangement contributing to the PES of dT_2^- is one molecule of thymidine interacting via its O8 atom with the hydroxyl group of the sugar moiety of the second nucleoside and is not stabilized by electron-induced intermolecular or intramolecular PT.

METHODS

Experimental Details. Anion photoelectron spectroscopy (PES) is conducted by crossing a beam of mass-selected negative ions with fixed frequency photons and energy-analyzing the resultant photodetached electrons. This technique is governed by the energy-conserving relationship $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron-binding energy, and EKE is the measured electron kinetic energy. Our apparatus has been described previously but briefly consists of an ion source, linear time-of-flight mass selector (TOF-MS), a neodymium-doped yttrium/aluminum-garnet (Nd:YAG) photodetachment laser, and a magnetic bottle (MB) photoelectron spectrometer.³⁹ The instrumental resolution of our MB photoelectron spectrometer is approximately 35 meV at EKE = 1 eV. The third harmonic (355 nm, 3.493 eV) of a Nd:YAG laser was used to photodetach the thymidine homodimer anion (dT_2^-), and the photoelectron spectrum was calibrated against the known atomic lines of Cu^- .

The neutral thymidine sample was introduced into the gas phase using a novel pulsed infrared desorption–pulsed visible photoemission anion source. Low-power infrared laser pulses (1.17 eV/photon) from a Nd:YAG laser desorb the neutral nucleosides from a slowly moving graphite rod thinly coated with sample. Almost simultaneously, a pulse of 532 nm (2.33 eV/photon) from a second Nd:YAG laser strikes a rotating yttrium oxide disk, producing low-energy electrons that attach to the evaporated neutral species. This process is critical to the formation of the intact biomolecular anions. A 250 μs duration pulse of ultrahigh-purity (UHP) helium from a pulsed valve provides a collisionally cooled jet to carry away excess energy and guide the resulting anions ($(\text{thymine-H})^-$, $(\text{thymidine})^-$, and $(\text{thymidine})_2^-$, see Figure S1) into the mass spectrometer. The dT_2^- anions were then mass-selected, and the photoelectron spectrum was recorded.

Computational Details. We have applied the density functional theory method with Becke's three-parameter hybrid functional (B3LYP)^{40–42} and the 6-31++G** basis set.^{43,44} The usefulness of the B3LYP/6-31++G** method to describe intra- and intermolecular hydrogen bonds has been demonstrated through comparison with the second-order Møller–Plesset (MP2) predictions.⁴⁵ The ability of the B3LYP method to predict excess electron binding energies was reviewed, and the results were found to be satisfactory for the valence-bound (VB) molecular anions.⁴⁶

The relative energies (ΔE) and Gibbs free energies (ΔG) of neutral and anionic complexes are defined with respect to the energy of the most stable neutral or anionic configuration. The stabilization free energies (G_{stab}) of neutral complexes are calculated as the difference between the energy of the complex and the sum of the energies of the fully optimized isolated monomers. In the case of anion radical complexes, G_{stab} values are calculated as the difference between the energy of the anion radical complex and the sum of energies of the fully optimized isolated anionic and neutral monomers. This method of

estimation of G_{stab} is justified by the fact that in the studied anionic complexes the excess charge is localized entirely on one of the monomers.

The adiabatic electron affinities (AEA_G) are defined as the Gibbs free energies difference between the neutral and the anion for both species at their fully relaxed geometries. The free energies of the neutral and anionic species result from correcting the relevant values of electronic energies for zero-point vibration terms, thermal contributions to energy, the pV term, and the entropy terms. These terms were calculated in the rigid rotor–harmonic oscillator approximation at $T = 298\text{ K}$ and $p = 1\text{ atm}$. Electron vertical detachment energies (VDEs) are defined as the energy of neutral dimer minus the energy of the anionic dimer at the geometry of the fully relaxed anion and can be directly observed in photoelectron spectroscopy experiments. The vertical electron affinities (VEAs) are the energy of neutral dimer minus the energy of the anion dimer both at the fully relaxed neutral geometry.

In past calculations, it has been shown that the B3LYP/6-31++G** VDEs⁴⁷ of the valence-bound clusters remain in good accordance with those extracted from the PES, an example being $(\text{uracil}\cdots\text{water})^-$. For such systems the B3LYP/6-31++G** approach appeared to be as good as the MP2/6-31++G(2df,2p)/MP2/6-311++G** level of theory.⁴⁸ Our theoretical investigation of dT_2^- was preceded by the calculations for the accessible combinations of neutral homodimers. For construction of the starting geometries of neutral complexes, we reoptimized, at the B3LYP/6-31++G** level, the geometry of neutral monomeric thymidine reported by Yurenko et al. as the most stable conformer in the gas phase at 420 K.⁴⁹ As pointed out by Shishkin et al.,⁵⁰ the flexibility of the nucleosides results in their conformational diversity depending on many, and sometimes unpredictable, factors. Therefore, absolute trust in the geometries from crystals or liquids may lead to uncertainties. The B3LYP optimized geometry of the monomer closely resembles its structure from previous DFT/DZP++ studies on the neutral and anionic forms of nucleosides,⁵¹ and the values of AEA_G and VDEs of thymidine reported by Richardson et al. are in good agreement with experimental values.³⁸

The geometries presented here have been fully optimized without geometrical constraints, and the analysis of harmonic frequencies proved that all of them are also geometrically stable (all force constants were positive). All computational calculations have been carried out with the Gaussian 03⁵² and Gaussian 09⁵³ codes. The pictures of structures and molecular orbitals were plotted with the GaussView 4.1 program.⁵⁴

RESULTS

Photoelectron Results. The photoelectron spectrum of the thymidine homodimer anion (dT_2^-) is presented in Figure 1. The onset of the spectrum occurs at EBE $\sim 1.1\text{ eV}$. This threshold value is an approximation of the AEA_G . The spectrum features a broad peak over the range of 1.9–2.2 eV, with a maximum at $\sim 2\text{ eV}$, which corresponds to the experimental VDE. The shape of the PES indicates dT_2^- exists as a stable valence-bound anion, and the broad spectral features suggest the presence of more than one anion radical structure.

Computational Results. Structures and Energetics of the Neutral Homodimers. The geometries of the neutral dT_2 complexes optimized at the B3LYP/6-31++G** level are presented in Figure 2. These dimers were found to be stabilized through hydrogen bonds between the thymidine monomers

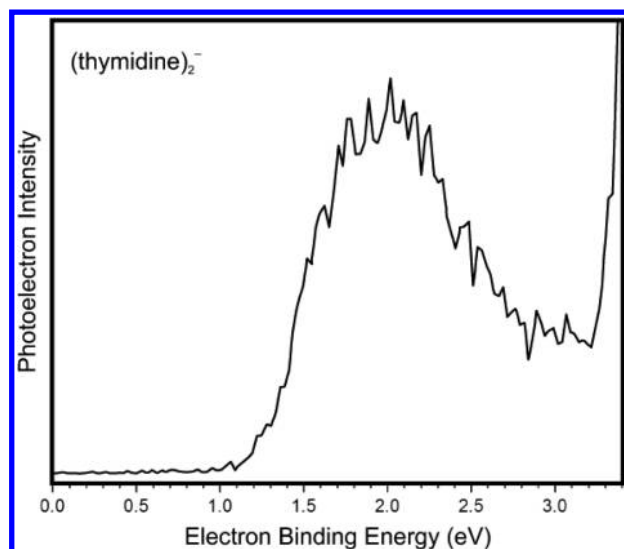


Figure 1. Photoelectron spectrum of thymidine₂[−] recorded with 3.49 eV photons.

and exist in two structural arrangements. Complexes where two hydrogen bonds are formed between the proton donor (H–N3) and the proton acceptors (O7 and O8 atoms) sites on the nucleobases in dT₂ will be referred to as the thymine⋯thymine configurations. Structures where a proton acceptor site from the thymine moiety of one nucleoside interacts with the sugar's 3'-OH proton donor group from the deoxyribose of the second

thymidine monomer to form a hydrogen bond will be referred to as the thymine⋯deoxyribose configurations.

Within the thymine⋯thymine family there are three conceivable hydrogen-bonded structures. In the two "symmetric" complexes, n_O8–O8 and n_O7–O7, two hydrogen bonds form between the identical donors/acceptor centers from each thymine monomer. In the n_O8–O7 structure, one thymine moiety employs the O7 and HN3 site and the other uses the O8 and HN3 center to form the two hydrogen bonds. For the thymine⋯deoxyribose configurations, geometry optimizations initiated from different starting structures, with a single hydrogen bond between the nucleosides at the O8–HO3' site, led to several minima of similar energy. Two structures (n1_O8 and n2_O8), bracketing the calculated geometrical and energetic characteristics, were chosen to best represent this family of configurations.

The relative energy (ΔE), Gibbs free energy (ΔG), vertical electron affinity (VEA), and stabilization free energy (G_{stab}) were calculated for each of the five neutral thymidine homodimers structures (Table 1). Despite the fact that the homodimers substantially differ geometrically from each other, their absolute energies and free energies lie within a quite narrow range, where the energy difference between the most (n_O8–O8) and least (n2_O8) stable structures is 3.3 and 2.7 kcal/mol, respectively. The G_{stab} values of −2.3, −0.8, and −0.4 kcal/mol suggest that the formation of neutral dimers in the gas phase is feasible when the complexes interact according to the thymine⋯thymine configuration. It can be expected that these complexes featuring two hydrogen bonds (n_OX–OX

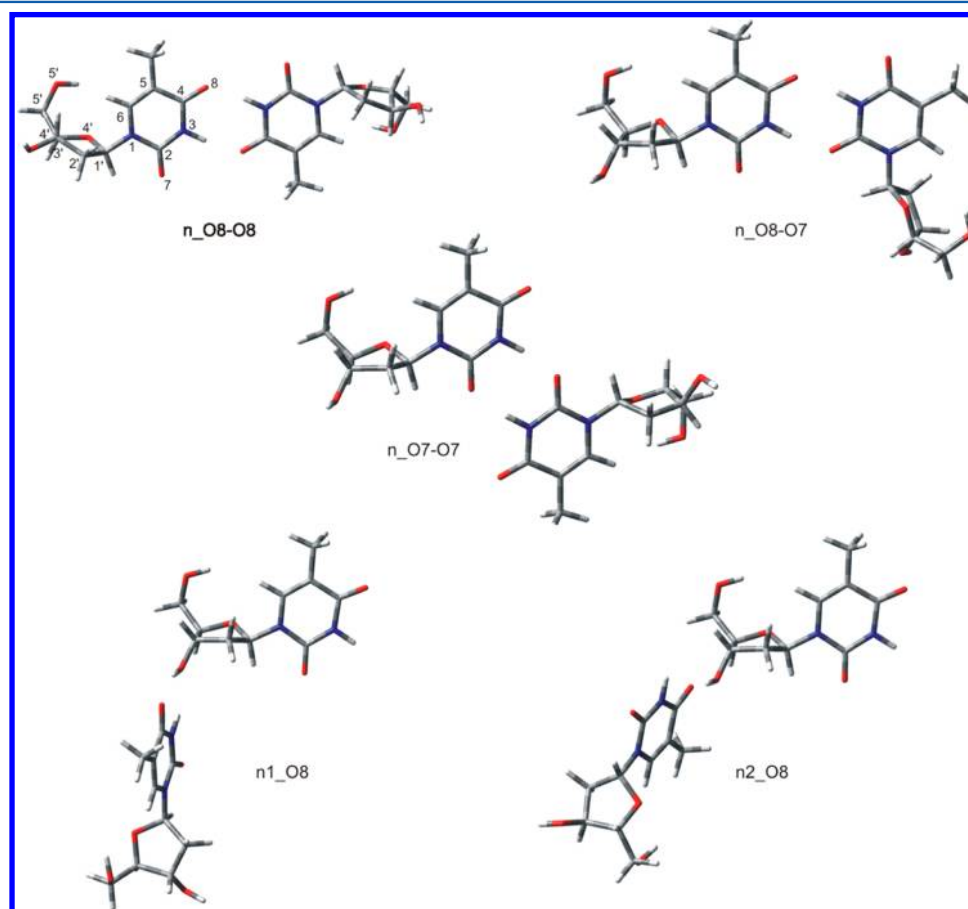


Figure 2. Structures of neutral conformations of thymidine₂ homodimers optimized at the B3LYP/6-31++G** level.

Table 1. Values of Relative Electronic Energy and Free Energy (ΔE and ΔG) with Respect to the Most Stable Neutral Thymidine Homodimer, Vertical Electron Affinities (VEA), and Stabilization Free Energies (G_{stab}) Calculated at the B3LYP/6-31++G** Level for the Neutral Thymidine Homodimers^a

complex	ΔE	ΔG	VEA	G_{stab}
n_O8–O8	0.00	0.00	0.33	−2.25
n_O8–O7	0.48	1.44	0.26	−0.81
n_O7–O7	0.93	1.89	0.22	−0.35
n1_O8	1.79	2.33	0.47	0.09
n2_O8	3.25	2.67	0.59	0.42

^a ΔE , ΔG , and G_{stab} values given in kcal/mol, VEA in eV.

structures, where X = O7 or O8) are more stable than the n1_O8 and n2_O8 complexes with a single hydrogen bond. The possibility of the thymine...deoxyribose configurations cannot be ruled out, however, considering that the n1_O8 and n2_O8 are only slightly less stable ($\Delta G = 2.3$ and 2.7 kcal/mol) than the most stable thymine...thymine configuration.

Structures and Energetics of the Anion Radical Homodimers. Calculations on the anion radicals were performed at the B3LYP/6-31++G** level of theory using the fully optimized neutral thymidine homodimer (dT₂) complexes resulting from the attachment of an excess electron as the starting point. The optimized geometries of seven anion radical homodimers, which originated from the five neutral parent complexes, are shown in Figure 3, and their corresponding calculated energies are summarized in Table 2.

Attachment of an electron to a given dT₂ neutral complex could result in two types of anion radicals: (1) a structure retaining the set of hydrogen bonds and (2) a structure in which intermolecular electron-induced proton transfer (PT) occurs (labeled with “-pt” suffix). Only the neutral structures from the thymine...thymine configurations n_O8–O8 and n_O8–O7 form both types of anions. For the remaining neutral structures, n_O7–O7, n1_O8, and n2_O8, upon the attachment of an excess electron only non-PT minima are found.

A common feature of all the studied dT₂[−] complexes is that the excess electron is localized on the π^* orbital of the thymine moiety in one of the monomers and the SOMO orbital is in a close resemblance with that of the valence anion of isolated thymine.^{8,9} These investigated anionic homodimer complexes, therefore, can be perceived as the thymidine valence anion solvated by the neutral thymidine. The heterocyclic ring of the thymine from the valence anion monomer undergoes folding which diminishes the antibonding repulsions of its nonplanar structure.

The most stable anions found were the thymine...deoxyribose structures, a1_O8 and a2_O8, with G_{stab} values of −11.6 and −12.3 kcal/mol, respectively. The remaining anionic complexes range in G_{stab} values from −4.4 to 0.2 kcal/mol. The difference in absolute energies and free energies between the most stable thymine...deoxyribose and thymine...thymine anions is approximately 8.6 and 7.2 kcal/mol, respectively.

The thymine...thymine structures, involving O8...HN3 hydrogen bonds, a_O8–O8 and a_O8–O7, along with the corresponding PT geometries a_O8–O8-pt and a_O8–O7-pt, are very close in energy ($\Delta E \sim 1$ kcal/mol). Both anionic complexes in which PT takes place are characterized by similar adiabatic electron affinities (AEA_G values ~ 0.6 eV) and similar

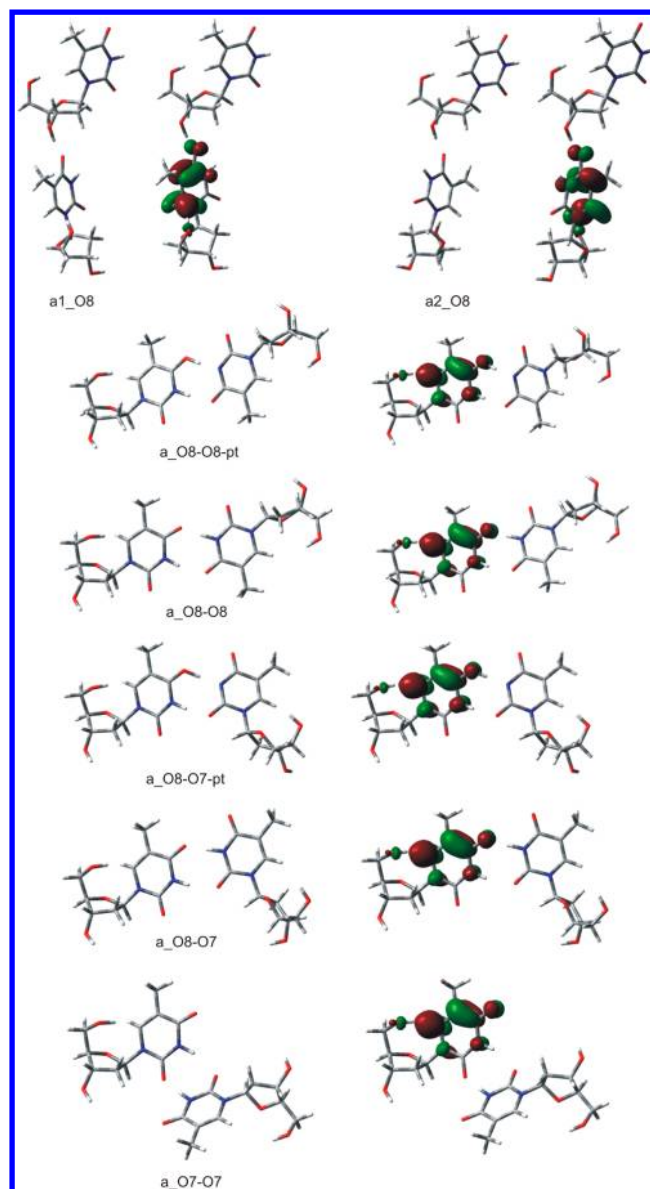


Figure 3. Structures of anion radical thymidine₂[−] homodimers optimized at the B3LYP/6-31++G** level and their singly occupied molecular orbitals plotted with a contour value of 0.05 bohr^{−3/2}.

Table 2. Values of Relative Electronic Energy and Free Energy (ΔE and ΔG with Respect to the Most Stable Dimer (a1_O8)), Stabilization Free Energy (G_{stab}), Adiabatic Electron Affinity (AEA_G) of the Corresponding Neutrals, and Vertical Detachment Energy (VDE) of the Anion Radical Thymidine Dimers Calculated at the B3LYP/6-31++G** Level^a

complex	ΔE	ΔG	G_{stab}	AEA _G	VDE
a1_O8	0.00	0.00	−11.58	1.04	2.03
a2_O8	0.14	−0.71	−12.30	1.07	2.04
a_O8–O8-pt	8.58	7.18	−4.40	0.61	2.31
a_O8–O8	9.58	8.88	−2.70	0.54	1.55
a_O8–O7-pt	8.85	8.50	−3.08	0.62	2.36
a_O8–O7	9.49	9.20	−2.38	0.59	1.60
a_O7–O7	12.27	11.82	0.24	0.49	1.44

^a ΔE , ΔG , and G_{stab} are given in kcal/mol, AEA_G and VDE in eV.

stabilization of the excess charge, reflected by VDEs of about 2.3 eV. The non-PT structures are weaker electron acceptors than their corresponding PT counterparts as they demonstrate slightly smaller electron affinities and considerably smaller VDEs. By comparing VDEs calculated for the PT structures and their non-PT counterparts, it can be seen that PT shifts the VDE values uniformly by about 0.76 eV. The anionic dimer a_O7–O7, stabilized by the O7...HN3 hydrogen bonds, cannot undergo electron-induced PT since the O7 site in the anionic thymine is deprived of excess charge. Based on relative energy and free energy, it is the least stable anionic complex.

Interestingly, the n1_O8 and n2_O8 neutral thymine...deoxyribose structures were the least stable among the considered neutral complexes but were found to be the most stable anions upon electron attachment. At first glance this finding seems surprising, but a1_O8 and a2_O8 are stabilized by a single hydrogen bond while two hydrogen bonds occur in the thymine...thymine geometries, e.g., in n_O8–O7. Dipole...monopole interactions are likely responsible for the observed effect. The direction of dipole moment in the thymidine (dT) molecule is shown in Figure S2. Hence, the positive pole of the dipole moment is relatively close and points to the region of negative charge in the n1_O8 or n1_O7 structures, while the opposite arrangement is characteristic of the thymine...thymine geometries (cf. Figure S2 with 3). As a consequence attractive dipole...monopole interactions are present in a1_O8 and a2_O8, while repulsive ones are present in the thymine...thymine geometries, which may explain the observed stability order.

DISCUSSION

The PES of dT_2^- presented provides experimental evidence of thymidine's ability to form adiabatically stable VB anion radical homodimers. Our computational modeling reveals that the most stable anionic homodimer complexes (a1_O8 and a2_O8) are the non-PT structures. The VDE values for the above-mentioned thymine...deoxyribose dimers are in excellent agreement with the position of the maximum of the PES signal at ~ 2 eV. The onset of the PES signal is around 1.1 eV and is in very good agreement with the theoretical AEA_G obtained for the most stable a1_O8 and a2_O8 geometries. The lack of PT in these structures may be explained by the weak acidity of the proton-donating hydroxyl group at the C3' position since the deprotonation enthalpy (DPE) of HO-C3' in the neutral nucleoside is calculated to be about 8 kcal/mol higher than the DPE of HN3.

The calculated VDE values of the PT complexes are comparable to the thymine...deoxyribose dimers, suggesting a similar magnitude of excess charge stabilization in the complexes. The calculated AEA_G values, however, confirmed that the anionic structures belonging to the thymine...thymine family were not populated under the experimental conditions. In the PES, no transitions were observed in the range of the theoretically predicted AEA_G for thymine...thymine structures (0.5–0.6 eV).

Interestingly enough, the PES of dT_2^- does not resemble that of previously registered PES for the anion homodimers of thymine and 1-methylthymine (T_2^- , 1-MeT_2^-) and isolated thymidine (dT^-) as presented in Figure 4. The anionic nucleoside homodimers can be considered as stabilized by a combination of hydrogen bond interactions and chemical modifications of a bare nucleobase. The stabilization effects in 1-MeT_2^- and dT^- can be related to the stability of the valence-

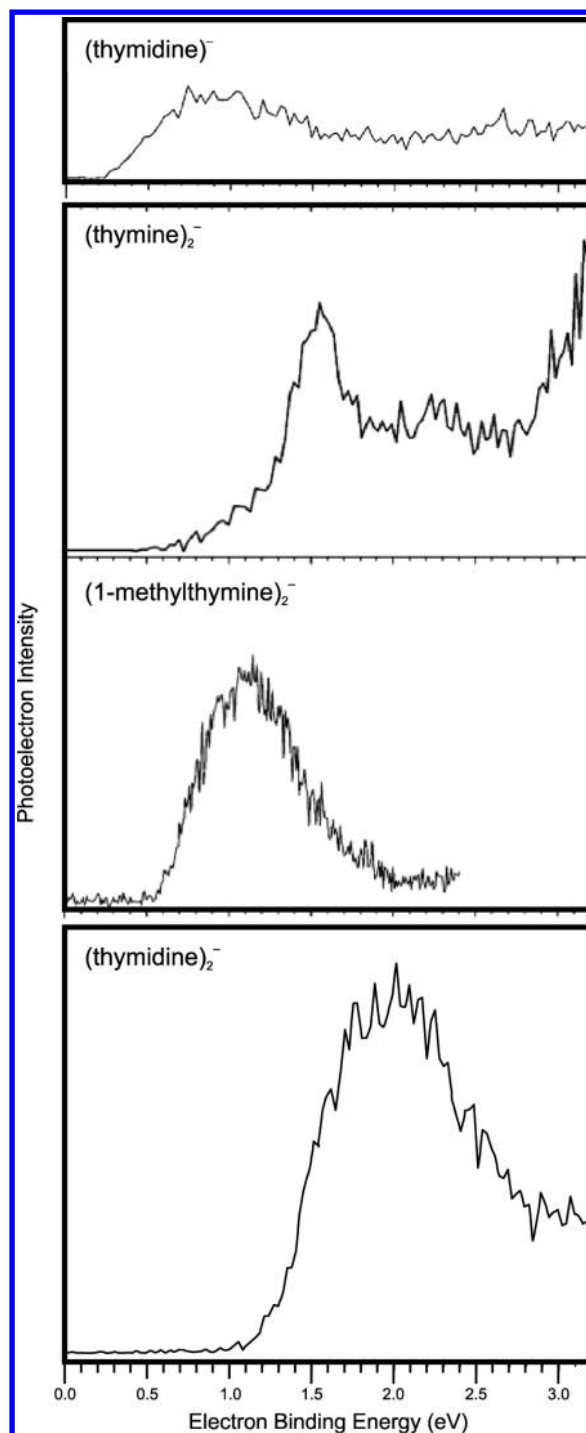


Figure 4. Comparison of the anion photoelectron spectra of thymidine $^-$ from ref 38, thymine $_2^-$ from ref 35, 1-methylthymine $_2^-$ from ref 35, and thymidine $_2^-$ from the current study, recorded with 3.49 eV photons.

bound anion of the isolated thymine (T^-). Since there is a lack of experimental data on the valence anion of T^- , we rely on the very accurate ab initio VDE value we obtained at the CCSD(T)/aug-cc-pVDZ level to estimate the shift from chemical modifications in the family of thymine homodimers.⁹ Comparing the computational VDE of 0.457 eV for T^- VB anion with the experimental VDE of 1.15 eV and then extracting from the PES of 1-MeT_2^- , we note that hydrogen bonding shifts the VDE value by ~ 0.69 eV toward higher EBES.

By comparing the VDE for T^- to that of dT^- , we estimate that chemical modification shifts the VDE value by ~ 0.43 eV toward higher EBES. Assuming that both effects are additive, one could estimate that the maximum of the PES signal for dT_2^- should be observed at ~ 1.6 eV. Although this value corresponds well to the calculated VDE for the a_{O8-O8} complex (1.55 eV), the experimental PES spectrum proves against this above prediction. The discrepancy between the estimated and experimental VDE values for dT_2^- is likely explained by stabilization interactions between the thymine...deoxyribose groups that are not present in the previous anionic systems with thymine moieties.

CONCLUSIONS

The thymidine homodimer anion (dT_2^-) was investigated using a combination of anion photoelectron spectroscopy and computational modeling. The photoelectron spectrum of the intact dT_2^- anion reveals a broad signal with a maximum at ~ 2.0 eV and a threshold at 1.1 eV. The significantly large electron vertical detachment energy indicates strong stabilization of the resulting complexes. Both the width of the band and its position are experimental evidence that shows that thymidine dimers form adiabatically stable valence-bound anions. The computational data obtained at the density functional theory level confirmed the existence of the stable valence anions of thymidine dimers in the gas phase. Moreover, we demonstrated that dimeric forms of thymidine display a significantly increased tendency to attach an excess electron in comparison to the isolated thymidine monomer. From our DFT calculations, the most stable radical anions are in the thymine...deoxyribose configuration, and in fact, these structures correspond to the VDE in the PES. Contrary to the previous studies on thymine complexes with various proton donors, we demonstrate here that the anion radical dimers featuring thymine...thymine interactions and their corresponding proton-transferred geometries are not found in the PES of dT_2^- .

ASSOCIATED CONTENT

Supporting Information

Orientation of dipole moment vector in the neutral thymidine molecule, mass spectrum of anions produced from thymidine, and complete refs 53 and 54. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: janusz@raptor.chem.univ.gda.pl (J.R.), kbowen@jhu.edu (K.H.B.).

Notes

The authors declare no competing financial interest.

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