J. Phys. Chem. A **1997,** *101,* 8335−8338 **8335**

Ab Initio Study on the Structure and Splitting of the Uracil Dimer Anion Radical

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Received: April 7, 1997⊗

As a model for the splitting of pyrimidine base pair defects by DNA photolyase, the uracil dimer and its anion radical have been studied by ab initio HF and MP2 methods. A transition state and an intermediate of the uracil dimer anion radical cleavage reaction have been located. The activation barrier for breaking the C5−C5′ bond in the dimer is found to be 6.2 kcal/mol at the UHF level. However, an MP2 single-point energy evaluation shows a vanishing barrier. The overall reaction energy for the dimer splitting is not significantly affected by electron attachment to the neutral dimer. In the dimer anion radical, the transition state, and the intermediate, the two pyrimidine rings differ substantially in their electronic and geometric structure. A one-step mechanism is proposed for the dimer splitting in the DNA photorepair process.

Introduction

Cyclobutane-type dimers of pyrimidine bases are formed by ultraviolet light damage to the DNA molecules. These lesions block the replication and the transcription of DNA and thus can be toxic to living cells. Utilizing the energy of an absorbed photon of near-UV light, the enzyme DNA photolyase is able to repair this damage by splitting the pyrimidine dimers.[1−7] Central to the enzymatic reaction is the cycloreversion step. Single-electron transfer from a reduced flavin cofactor to the pyrimidine dimer results in the dimer anion radical and initiates the splitting of the C5−C5′ and C6−C6′ bonds of the dimer.[1,5,7] Quantum chemical calculations can contribute to the understanding of the dimer cleavage reaction by determining the structure and energetics of the reaction species.[8−11]

Recently, we have considered in detail the splitting of pyrimidine dimers initiated by electron transfer using the semiempirical AM1 method.[11] In particular, it was shown that a dramatic reduction of the activation barrier for the cleavage reaction is caused by a single electron transfer to or from pyrimidine dimers. The sequence of the bond breaking in the dimer anion radical (first the C5−C5′, then the C6−C6′ bond) was found to be opposite to that in the cation radical. Solvation effects on the dimer splitting were found to increase the reaction barriers with the polarity of the environment.

Ab initio SCF calculations on the thymine dimer and its cation radical show that the puckering of the four-membered ring in the neutral and cationic dimers is an important feature of the dimer structure.[10] However, the semiempirical methods AM1 and PM3 predict the pyrimidine dimers' structures to have a planar four-membered ring,[9,11] at variance with the puckered ring found in the crystal structures of the uracil dimer[12] and of the photodimer of 1,3-dimethylthymine.[13]

Pyrimidine dimer anion radicals play a key role in the photoinduced DNA repair process, but no structural and energetic characteristics of these species are available so far from ab initio calculations. It was the goal of the present computational investigation to study in detail the structure and energetics of the uracil dimer U−U and its anion radical U−U$^-$, as well as transition states and possible intermediates formed in the course of the fragmentation reaction of the anion radical.−

TABLE 1: Adiabatic Electron Affinity (EA), Reaction Energy (Δ*E*), and Activation Barrier (Δ*E*‡) for the Uracil Dimer Cleavage and Reaction Energy for the Formation of the Intermediate (Δ*E*$_{\mathrm{Int}}$) and of Its Splitting to Monomers (Δ*E*$_{\mathrm{split}}$)[a]

	U−U			U−U$^-$			
method	EA	Δ*E*	Δ*E*‡	Δ*E*	Δ*E*‡	Δ*E*$_{\mathrm{int}}$	Δ*E*$_{\mathrm{split}}$
UHF	−1.24	−6.9	>36	−11.3	6.2	−26.3	15.0
MP2	−1.20	7.4		5.9	−1.1	−10.3	16.2

[a] EA in eV; energy changes Δ*E* in kcal/mol.

Calculation Method

The geometries of all molecules considered were optimized at the HF level with the help of the program GAUSSIAN92[14] using 6-31G* basis sets. No constraints were applied in the geometry optimizations. The transition-state structure was identified using geometries obtained by the reaction coordinate method as starting points. All stationary points were checked by a vibrational analysis. For an open-shell system, the spin-unrestricted Hartree−Fock method (UHF) was applied. To obtain more accurate energies including electron correlation, MP2 calculations were carried out. Although U−U may exist in six isomeric forms, the cis−syn isomer alone is significant for the photorepair reaction[1,2] and therefore it has been considered in the present study.

Results and Discussion

Does the Uracil Dimer Anion Radical Exist? According to the present calculations (Table 1), the neutral uracil dimer has a negative electron affinity (EA) in the gas phase. This implies the anion radical to be unstable; spontaneous detachment of an electron occurs, resulting in the neutral dimer. Therefore, the question arises whether theoretically evaluated properties and structural parameters for the dimer anion radical correspond to a real system or to a fictitious model. Recently, this question has been studied for pyrimidine monomers, both theoretically[15−18] and experimentally.[19−21] One considers two types of states of anion radicals: (1) conventional or covalent anionic states in which the excess electron is delocalized over valence orbitals of the molecule and (2) dipole-bound anions where the excess electron is localized outside the molecular frame and is bound by the electric field of a polar molecule. A molecular dipole moment larger than 2.5 D is required to trap an electron in a

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⊗ Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S1089-5639(97)01187-0 CCC: $14.00

potential well and to form such a dipole-bound anion.[22] According to our calculation, the dipole moment of U−U is 6.85 D and, consequently, it is sufficiently high to ensure the existence of a dipole-bound anionic state. On the basis of SCF and MP2 calculations, it was suggested that by electron attachment to uracil or uracil−water complexes the excess electron is bound by the dipole field of the polar molecule and no covalent anions are formed.[17,18] However, according to those calculations, part of the excess electron charge density is localized around the atoms in the dipole-bound states, giving the anion a partially covalent character.[17] Dipole-bound anions of uracil and thymine were also detected experimentally.[19,20] On the other hand, the existence of covalent anion states for uracil and thymine was predicted using a scaling procedure for calculated electron affinities.[15] On the basis of experimental data, it has been concluded that covalent anions can be formed in addition to the dipole-bound anions and that covalent anions become more favored with increasing molecule size.[20,21]

It is a difficult problem to obtain precise values for the electron affinity of pyrimidine dimers using ab initio methods. We found that UHF and MP2 adiabatic EA values of the uracil dimer, −1.20 and −1.24 eV (Table 1), respectively, are similar to those of the uracil monomer, −1.16 eV (HF) and −1.10 eV (MP2). To produce a reasonable value of EA for U−U, the scaling procedure[15] may be applied. One expects[15] the adiabatic EA value of U−U to be 0.2−0.3 eV, slightly less than the predicted EA value for uracil of 0.4 eV.

A polar medium is known to significantly stabilize the pyrimidine anion radicals against dissociation into a solvated electron and a neutral molecule.[23] Recently, experiments using photochemically induced dynamic nuclear polarization (photo CIDNP) have provided evidence for the existence of the valence pyrimidine dimer and monomer anion radical.[24] Thus, despite negative electron affinities produced by the present HF and MP2 calculations for U−U, the corresponding anion radical seems to exist, while the dipole-bound anions may act as temporary precursors for electron attachment to the neutral species in a nonpolar environment.

Energetics. The energy changes associated with the dimer-splitting reaction are listed in Table 1. Different from the cyclobutane cleavage, which is known to be clearly endothermic (the experimental reaction energy[25] being 18.2 kcal/mol), the U−U splitting reaction is exothermic at the HF level and less endothermic at the MP2 level owing to a relative destabilization of the four-membered ring by the uracil fragments. According to our calculations, a single electron transfer to U−U does not strongly affect the reaction energy. The cleavage of the dimer anion radical is calculated at the HF level to be 4.4 kcal/mol more exothermic than that of the neutral dimer (Table 1), but the difference in MP2 reaction energies is only 1.5 kcal/mol. This small effect of the electron transfer on the overall fragmentation enthalpy for U−U is in line with previous results.[11]

The uracil dimer splitting bears some similarity to the cycloreversion of cyclobutane. For the latter molecule, a concerted cleavage reaction is forbidden according to the Woodward−Hoffmann rules[26] and is thus expected to have a high activation energy. A thorough analysis of nonpolar cycloaddition based on MCSCF calculations leads to the conclusion that the reaction proceeds in a stepwise fashion and that the corresponding reaction barriers are high, about 40−60 kcal/mol.[27−30] We were unable to locate the transition state for the cleavage of the neutral uracil dimer because of poor SCF convergence. However, our calculations of several points along the reaction path indicate that the activation barrier is higher than 36 kcal/mol, and therefore, the neutral dimer is kinetically stable, in line with experimental observations.[4]

By contrast, pyrimidine dimer anion radicals are highly reactive species that undergo a facile cleavage reaction in a stepwise fashion.[1−5] AM1 calculations have shown that the cleavage reaction of the anion radical is initiated by breaking the bond C5−C5′, which leads to an intermediate held together by the C6−C6′ bond.[11] In the present calculations, the transition-state structure for the C5−C5′ bond splitting found with the reaction coordinate method was improved with the help of the eigenmode following method.[14] A vibrational analysis of the transition state yields one imaginary frequency of 689i cm^{-1}. The activation energy $\Delta E^{\ddagger}$ found at the HF level is quite low, only about 6 kcal/mol (Table 1). MP2 corrections lead to the complete disappearance of the barrier. Taking into account that MP2 often overcorrects the HF energy,[31] one expects that the activation energy for the splitting reaction is very low (presumably less than 3 kcal/mol). Therefore, we conclude that the anion U−U^- is highly reactive and undergoes a facile cleavage. Thus, although electron transfer to U−U does not have a large effect on the overall energy change during the cleavage reaction, the reactivity of the dimer is changed dramatically. The intermediate formed by the C5−C5′ bond splitting in the dimer anion radical is found to be energetically favored over both the parent dimer and product monomers (see Table 1 for the energy changes of the formation, ΔE_{int}, and splitting, ΔE_{split}, of the intermediate). HF and MP2 calculations give similar values ΔE_{split} for the energy change that accompanies the splitting of the intermediate into neutral and anionic uracil molecules (15−16 kcal/mol). Attempts to localize a transition state that separates the intermediate and the products failed. Two points should be noted in this context. First, no evidence for the existence of a long-lived intermediate has been experimentally obtained.[24] Second, AM1 calculations predict that the splitting of the first bond rather than the cleavage of the second bond in pyrimidine dimers determines the reaction rate.[11]

In principle, the cleavage of the dimer anion may also be initiated by breaking the C6−C6′ bond, which leads to a different intermediate where two uracil rings are linked by the C5−C5′ bond. However, MP2 calculations indicate that the formation of this intermediate is endothermic by 24.3 kcal/mol, and consequently, this alternative reaction path is unlikely. This result is completely in line with those of our previous study.[11]

In the gas phase the entropy term ($-T\Delta S$) considerably contributes to the free energy of the splitting reaction. It is about −14 kcal/mol for the splitting of both the dimer and the intermediate and mainly due to translational and rotational contributions.[11] However, in the DNA−photolyase complex, these degrees of freedom do not contribute to the reaction entropy and the resulting $T\Delta S$ value due to changes in the vibrational entropy amounts to only about −3 kcal/mol.[11] Thus, the free energy changes associated with the uracil dimer splitting is predicted to be close to zero if the MP2 value of the reaction energy is used. This conclusion is in line with recent experiments[24] that have demonstrated that the interconversion of the pyrimidine monomer and dimer anion radicals is reversible, indicative of a low absolute value of free energy for the splitting reaction. However, the free energy for cleaving the intermediate remains clearly positive (about 13 kcal/mol), and the intermediate is thus rather stable. On the other hand, the structure of the intermediate differs considerably from that of the parent dimer anion radical (parts B and D of Figure 1). Most important is that the uracil rings of the intermediate are rotated relative to each other around the C6−C6′ bond. Therefore, steric constraints for the intermediate structure in the enzyme−substrate

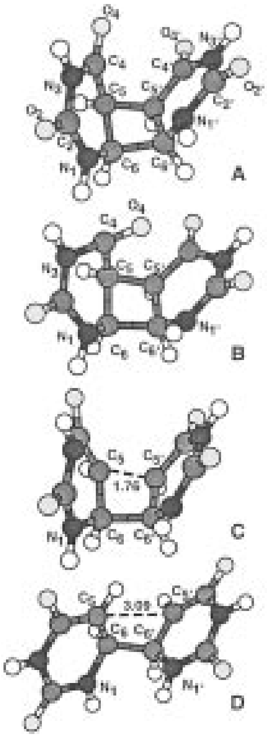

Figure 1. Calculated structures of the uracil dimer (A), its anion radical (B), a the transition state (C), and the intermediate (D) of the splitting reaction of the dimer anion radical.

TABLE 2: Structures of the Four-Membered Ring of the Uracil Dimer U−U, Its Anion Radical U−U⁻, the Transition State TS, and the Intermediate Int of the Splitting Reaction of U−U⁻

	U−U	U−U⁻	TS	Int
	Bond Lengths (Å)			
C5−C5′	1.553	1.551	1.763	3.088
C5′−C6′	1.539	1.540	1.526	1.494
C6−C6′	1.553	1.552	1.553	1.554
C5−C6	1.537	1.549	1.539	1.492
	Bond Angles (deg)			
∠C6−C5−C5′	87.5	88.0	84.0	54.3
∠C5−C5′−C6′	88.6	90.0	86.2	54.7
∠C5′−C6′−C6	87.5	88.3	91.9	111.9
∠C5−C6−C6′	88.1	89.6	93.5	112.8
∠C5−C5′−C6′−C6	20.5	15.5	15.3	30.1

complex are expected. They can hinder a complete relaxation of the structure and in this way increase the energy of the intermediate in the enzymatic photorepair process. The destabilization of the intermediate can switch the splitting reaction mechanism from a two-step to a one-step reaction. To estimate the activation barrier for such a one-step cleavage, we have computed a conceivable structure where both C5−C5′ and C6−C6′ bond lengths are fixed at 1.763 Å as found in the true transition state for the C5−C5′ bond cleavage (see the next section and Figure 1C). All other degrees of freedom were optimized. According to MP2 calculations, the energy of this structure is 6.0 kcal/mol higher than that of the parent dimer anion radical. Therefore, one can assume that the activation barrier for the one-step splitting is low enough for the reaction to proceed at a relatively fast rate. Otherwise, i.e., in case of a two-step mechanism, one has to identify a source providing the energy required for splitting of the intermediate. The present calculations were performed for an isolated uracil dimer, neglecting any influence of the protein environment corresponding to the actual photorepair process. However, relative destabilization of the intermediate in the photolyase active site by about 13 kcal/mol seems unlikely. In conclusion, the cleavage of the pyrimidine dimer anion radicals by the enzyme DNA−photolyase appears to occur without formation of the intermediate.

Structures. The optimized structure of cis−syn U−U is shown in Figure 1A. No experimental data are available for the structure of U−U in the gas phase; however, the crystal structure of the cis−syn dimer of U−U is known.[12] When comparing calculated and crystal data, one should keep in mind that a strong three-dimensional network of hydrogen bonds is formed in the crystal between a dimer and six of its neighbors (average bond length of 2.9 Å).[12] This may considerably affect the geometry of the dimer in the crystal compared to that in the gas phase.

An important structural feature of the dimer is the four-membered cyclobutane-like ring (see Table 2). Our HF calculations predict a puckered ring structure with a dihedral angle C5−C5′−C6′−C6 of 20.5°, in satisfactory agreement with the experimental value of 25.0° [12] and the corresponding dihedral angle calculated at the HF/6-31G level for the thymine dimer (17.9°).[10] The puckering of the four-membered ring causes a distortion of the U−U structure and results in slightly different geometries of the two uracil rings in the dimer. The most noteworthy geometric parameters are compared in Table 3. The uracil rings in the dimer are not planar; the dihedral angle C6−C5−C4−N3 is found to be −27.0°, whereas the corresponding angle in the other ring (C6′−C5′−C4′−N3′) amounts to −15.5°. These rings are twisted relative to one another; the calculated dihedral angle C4−C5−C5′−C4′ of −27.6° is somewhat larger than that of −23.0° found in the crystal structure.[12] Calculated bond lengths and bond angles are in good agreement with experimentally observed geometric parameters. Overall, the structure of U−U is very similar to that computed for the thymine dimer.[10] Inversion of the cyclobutane ring of U−U results in another conformer, a mirror image of the parent structure. We found the barrier between these two conformers to be 4.9 and 6.9 kcal/mol at the HF and MP2 levels, respectively.

TABLE 3: Mulliken Charge (*Q*) and Geometrical Parameters of the Uracil Rings 1 and 2 in U−U, U−U⁻, the Transition State TS, and the Intermediate Int

	U−U		U−U⁻		TS		Int	
ring	1	2	1	2	1	2	1	2
			Mulliken Charge (au)					
Q	0.03	−0.03	−0.81	−0.19	−0.66	−0.34	−0.86	−0.14
			Bond Lengths (Å)					
C4−O4	1.119	1.188	1.272	1.195	1.250	1.202	1.231	1.205
C5−C4	1.513	1.509	1.525	1.507	1.447	1.467	1.377	1.444
C4−N3	1.372	1.374	1.481	1.382	1.455	1.384	1.434	1.388
			Bond Angles (deg)					
∠C6−C5−C4	113.5	117.5	112.4	116.4	115.0	119.3	123.4	121.9
∠C5−C4−N3	115.2	114.5	106.3	114.9	114.7	114.8	115.2	115.3
∠C6−C5−C4−N3	−27.0	−14.5	−47.5	−2.4	16.4	−20.2	−3.0	5.3
∠C6−C5−C4−O4	156.7	162.0	89.0	168.4	178.3	161.0	177.4	186.3

The formation of the anion radical U−U$^-$ by attachment of an electron to U−U leads to considerable structural changes (see Figure 1B and Tables 2 and 3). Although the electronic charge distribution in the neutral dimer is almost symmetric, one calculates a clear localization of the ionic charge on one of two fragments of the anion U−U$^-$: $q(\mathrm{U}) = -0.81$, $q(\mathrm{U}') = -0.19$ (Table 3). This charge separation is very similar to that found in AM1 calculations.[11] The large difference in the charge distribution is associated with an asymmetric structure of the anion radical. Attachment of a single electron to U−U facilitates the C5−C5′ bond splitting significantly, as found in experiment[24] as well as in the present (Table 1) and previous calculations;[11] however, it hardly affects the bond distances in the cyclobutane ring (Table 2). By contrast, activation of the C6−C6′ bond cleavage due to removal of an electron from the dimer is associated with a considerable lengthening of the corresponding bond distance.[10,11] In U−U$^-$ the puckering of the cyclobutane ring is less pronounced than in the neutral dimer, the dihedral angle C5−C5′−C6′−C6 being about 15°. Since the anionic charge in U−U$^-$ is localized to a considerable extent on one of the two C4═O4 groups, it is not surprising to find the most pronounced structural changes in the vicinity of this group. The strongly elongated C4═O4 bond is oriented almost perpendicular to the plane defined by the atoms N3, C5, and C6 of the uracil ring (see Figure 1B). The dihedral angles O4−C4−C5−C6 and O4−C4−N3−C2 are 89.0° and −86.5°, respectively, while the bond angles ∠O4−C4−C5 (119.4°) and ∠O4−C4−N3 (117.9°) are rather close to the standard value of 120°. Compared to the neutral dimer, the C5−C4 and C4−N3 distances are lengthened and the bond angle ∠C5−C4−N3 is decreased, indicative of a reduced π-conjugation in the ring. The dihedral angle C6−C5−C4−N3 of −47.5° indicates a considerable distortion of the ring from planarity; the other uracil ring in the dimer anion has a regular geometry.

Finally, we consider the changes of the U−U$^-$ geometry caused by breaking the C5−C5′ bond. The structure of the corresponding transition state is shown in Figure 1C. The formation of the transition state is associated with a moderate increase of the C5−C5′ bond length (by only about 0.2 Å) compared to the dimer anion. The other bond distances and angles of the cyclobutane-like ring remain almost unchanged (Table 2). A less asymmetric distribution of the electron charge over both uracil rings in the transition state is associated with rather similar geometries for both moieties (Table 3).

In the intermediate formed after the C5−C5′ splitting, the uracil rings are twisted relative to each other by a 67° rotation around the C6−C6′ bond. Like the reactant U−U$^-$, the intermediate has a pronounced asymmetric charge distribution between the fragments (Table 3). The essentially planar structure of the uracil fragments is associated with an improved intra-ring π-conjugation, in line with the remarkable stability of the intermediate with respect to the reactant. Thus, the delocalization of the negative charge over both rings in the transition state seems to be the main cause for the drastic reduction of the activation barrier in the dimer anion radical.

Conclusions

Using HF and MP2 calculations, we have studied the structures of the uracil cis−syn dimer and its anion radical, as well as of the transition state and the intermediate for the C5−C5′ bond-splitting reaction in the anionic dimer. The cleavage of the bond in U−U$^-$ is associated with a low activation barrier estimated to be less than 3 kcal/mol, whereas the activation energy of the cycloreversion reaction in the neutral dimer seems to be higher than 36 kcal/mol. Despite the dramatic effect of the electron attachment on the reactivity of the uracil dimer, there is no considerable change in the free energy of the dimer-splitting reaction. The calculations predict large differences between the uracil rings of U−U$^-$ for the electron density distribution and the geometry. The dimer anion radical has a very pronounced asymmetric structure. On the basis of the calculated energies, we propose that the cleavage of the dimer anion radical occurs as a one-step reaction in the active site of the enzyme DNA−photolyase.

Acknowledgment. We thank M.-E. Michel-Beyerle for her continued interest in our work and for many stimulating discussions. N.R. thanks M. C. Zerner for his hospitality at the Quantum Theory Project, University of Florida, where the paper was cast into its final form. This work has been supported by the Deutsche Forschungsgemeinschaft through SFB 377 and the Fonds der Chemischen Industrie.

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