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Photoinduced Hydrogen Atom Transfer of Free-Base Porphin

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We present results of a theoretical study on the photoinduced hydrogen atom transfer reaction in free-base porphin. Electronic structure calculations using density functional theory (DFT) with Becke's three-parameter hybrid functional are carried out to predict the structures and energetics for the low-lying triplet states of free-base porphin isomers. Transtion state searches were also carried out to locate the structures and barriers of the cis−trans and trans−trans transition states. Our results support the proposal that the trans−trans hydrogen transfer occurs on the triplet potential energy surface (PES) in a stepwise fashion through a cis isomer. After being excited from the ground state, the molecule is predicted to move into the trans $T_2(^3B_{1u})$ state on the triplet PES and undergoes trans−cis isomerization. The cis−trans isomerization reaction is predicted to occur primarily on the $^3A'$ PES and produces the lowest triplet trans $T_1(^3B_{2u})$.

I. Introduction

The triplet excited state of porphyrins is important in photodynamic therapy,[1] optical recording,[2] and optical limiting[3,4] applications. For the unsubstituted free-base porphyrin (porphin, PH_2), the inner-hydrogen atom transfer (IHAT) reaction in the ground state has been a subject of numerous theoretical[5−7] and experimental[8−11] studies. Likewise, there are important issues to be resolved for the parent compound in the excited state. This work focuses on the mechanism of the photoinduced IHAT of free-base porphin observed in the triplet excited state.[12−15] In contrast to the established hydrogen transfer mechanism in the ground state, the corresponding photoinduced process is not well understood. The photoinduced IHAT in porphyrins and derivatives was first observed by Zalesskii et al.[16] The photoisomerization for the parent compound was reported by van Dorp et al.[12,13] and Volker and van der Waals.[14] The experimental studies by van der Waals and co-workers have shown that the photoisomerization occurs at a temperature as low as 1.3 K following laser excitation from the ground into the first singlet excited state (S_1). Furthermore, no significant enhancement in the reaction rate was observed at 77 K or by exciting to the higher energy Soret band. Therefore, it was speculated that the photoreaction may be associated with the vibrational relaxation that follows the intersystem crossing (IC) from S_1/T_1 into T_1/S_0 where coupling of the two lowest triplet states may lead to the displacement of the inner protons.[14] An alternate mechanism has also been proposed[15,17] for the photoreaction that involves a metastable cis tautomer on the triplet PES. This proposed photoreaction mechanism is similar to the generally accepted ground-state IHAT mechanism of free-base porphin. However, experimental data[15] have suggested that the triplet cis tautomer is lower in energy than the corresponding trans configuration. In this model the trans species would tautomerize to the cis by proton tunneling and, at higher temperature, by energy barrier crossing. This is followed by fast intersystem crossing from the cis isomer to the ground state that is promoted by the smaller T_1-S_0 gap.[15,17]

We are unaware of any theoretical studies aimed at unraveling the mechanism of the photoinduced IHAT reaction in free-base porphin. To shed more light on this process, electronic structure calculations were carried out to characterize the structures and energetics of minima and transition states for the inner-hydrogen migration on the triplet PES of free-base porphin.

II. Computational Methods

The structures of all stationary points have been predicted using the Kohn−Sham (KS)[18] density functional theory with the 6-31G(d)[19,20] basis set. DFT calculations were carried out using Becke's three-parameter (B3LYP) hybrid functional.[21−23] Open-shell DFT calculations for the triplets were carried out using the unrestricted SCF method.[24] The structures were verified to be either minima or transition states by evaluating the appropriate matrix of energy second derivatives (Hessian). In addition, single point calculations were also carried out using the larger 6-311+G(2d,p)[25,26] basis set to gauge effect of basis set on the energetics for selected stationary points on the PES. A comparison of the two sets of DFT calculations suggests that the energetics have basically converged. Unless mentioned otherwise, the results of the B3LYP/6-31G(d) level are used for discussions of the energetics throughout. Previously, we[4] and others[7,27,28] have shown that this level of theory produced structure and vibrational frequencies of PH_2 that are quite reliable. The B3LYP/6-31G(d) ground-state IHAT barrier[7] and the S_0-T_1 gap[4] for PH_2 were also reported to be in excellent agreement with experiment. All electronic structure calculations were carried out using the Gaussian 98[29] program.

III. Results and Discussion

The optimized B3LYP/6-31G(d) structures are displayed in Figure 1 with selected geometrical parameters. The search for metastable triplet states of PH_2 included two electronic states obtained by exciting between Gouterman's four orbitals (two top filled MOs and two lower virtual ones). These excitations give rise to four structures, two minima and two transition states, of the $^3B_{2u}$ and $^3B_{1u}$ electronic states. The structure of the lowest

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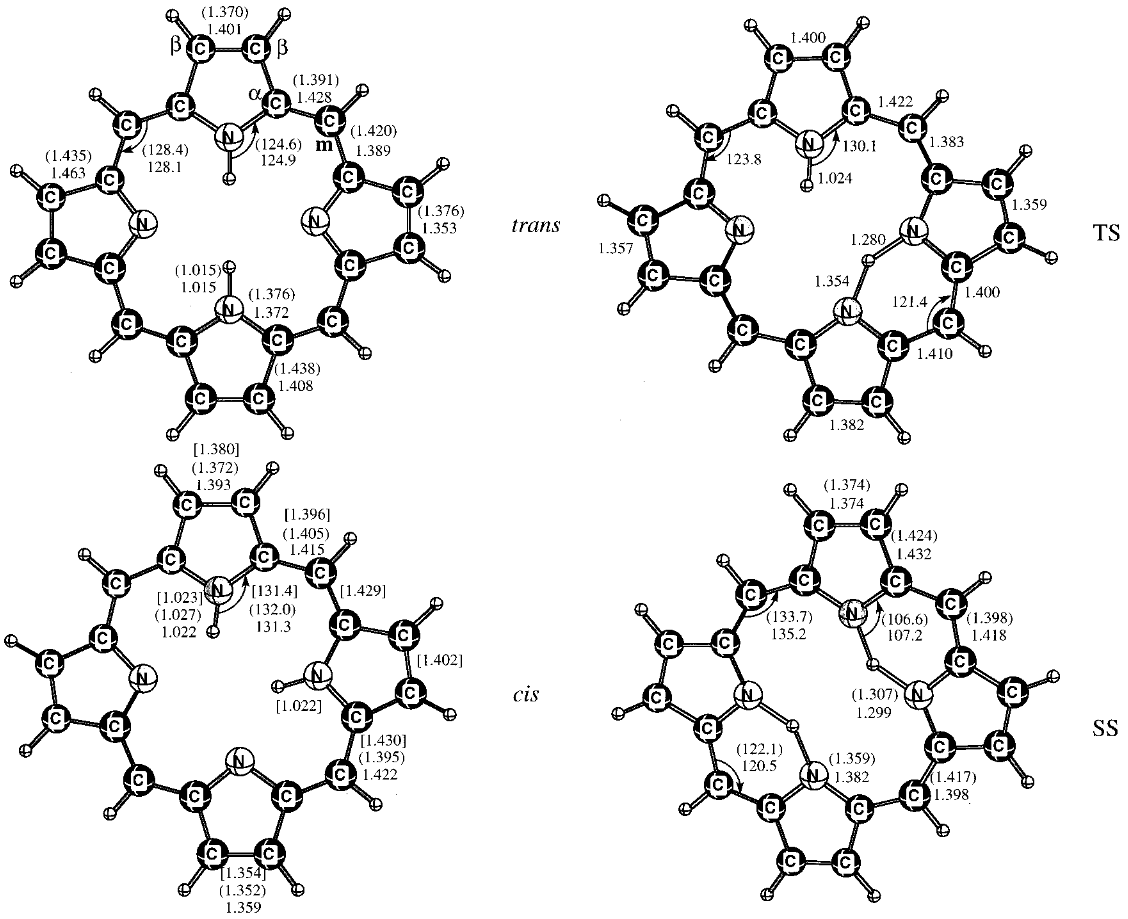

Figure 1. B3LYP/6-31G(d) geometric parameters (bond lengths in angstroms, angles in degrees) for the trans ($^3B_{2u}$), cis ($^3A_1$), TS ($^3A'$), and SS ($^3B_{1u}$). The corresponding parameters of the low-lying excited states, cis ($^3B_2$), trans ($^3B_{1u}$), and SS ($^3B_{2u}$) are in parentheses. Structural parameters for the cis ($^3A'$) are in brackets. Cartesian coordinates are available in the Supporting Information.

triplet excited state for the *trans*-PH_2 has been determined at the B3LYP/6-31G(d) level previously.[4] The computed triplet−triplet excitation energies and the S_0−T_1 gap of the lowest triplet ($^3B_{2u}$) are in excellent agreement with experiment. The details of the geometry, energetics (relative to S_0), and spectra of low-lying excited states are presented elsewhere.[30] The two lowest excited states relevant to the photoinduced IHAT reaction are shown in Figure 1. They are found to retain D_{2h} symmetry. There are only small changes in structure and energetics going from T_1 to T_2. Noticeable changes are observed for the C−C bond distances. Upon going from T_1 to T_2, the C_α−C_β and C_β−C_β bonds in the two pyrrole rings with inner hydrogens are slightly (0.03 Å) lengthened and shortened, respectively, by about the same amount. In contrast, the C_α−C_β and C_β−C_β bonds in the other two pyrrole rings are slightly shortened and lengthened, respectively. In addition, one of the C_α−C_m bonds increases while the other decreases in distance. These structural changes resulted in a modest increase in energy, about 6 kcal/mol for T_2 relative to T_1 (Table 1).

To explore the concerted and stepwise inner-hydrogen atom transfer reactions, the cis, doubly bridged (SS), and cis−trans transition state (TS) are considered. For the C_{2v} cis tautomer, the lowest state is of $^3A_1$ symmetry, lying at 10.0 kcal/mol above the lowest trans configuration. The next electronic state (cis ($^3B_2$)) is located at 20.0 kcal/mol on the classical PES. The $^3A_1$ and $^3B_2$ cis isomers are not local minima but transition states with an imaginary frequency of 429i and 1574i cm^{-1}, respectively. The lowest cis local minimum is of $^3A'$ symmetry. It is only slightly lower in energy than the lowest C_{2v} structure. Energetically, it is located 9.9 kcal/mol above the trans form. This is reduced to 9.2 kcal/mol, after zero-point energy corrections were included. Therefore, our results for the *cis*-PH_2 form suggest that the observed phosphorescence and T_1−S_0 radiationless decay are likely to originate from the trans isomer, and not the cis form, as previously postulated.[15,17] Although there is a small difference in energy between C_{2v} cis($^3A_1$) and C_s cis($^3A'$), significant structural distortions are found. As

TABLE 1: Total and Relative Energy (Classical = ΔE and Zero-Point-Corrected = ΔH^0) for the Cis, Trans, Transition State (TS), and a Second-Order Stationary (SS) Point

structure	total energy	$\langle s^2 \rangle$	ΔE	ΔH^0
	B3LYP/6-31G(d)			
trans (1^3B_{2u})	−989.49504	2.06	0.0	0.0
trans (1^3B_{1u})	−989.48571	2.04	5.8	5.8
cis ($^3A_1$)	−989.47905	2.05	10.0	8.3[a]
cis ($^3B_2$)	−989.46311	2.03	20.0	19.5[b]
cis ($^3A'$)	−989.47920	2.06	9.9	9.2
TS($^3A'$)	−989.46423	2.05	19.3	16.0[c]
SS($^3B_{2u}$)	−989.44266	2.04	32.9	24.3[d]
SS($^3B_{1u}$)	−989.44866	2.04	23.3	21.8[e]
	B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d)			
trans ($^3B_{2u}$)	−989.76625	2.06	0.0	0.0
trans ($^3B_{1u}$)	−989.75742	2.04	5.5	5.5
cis ($^3A'$)	−989.75070	2.05	9.8	9.1
TS($^3A'$)	−989.73739	2.04	18.1	14.8

[a] Zero-point corrections exclude one imaginary frequency of 429i cm^{-1}. [b] Zero-point corrections exclude one imaginary frequency of 1574i cm^{-1}. [c] Zero-point corrections exclude one imaginary frequency of 1630i cm^{-1}. [d] Zero-point corrections exclude three imaginary frequencies of 3011i, 1672i, 1620i cm^{-1}. [e] Zero-point corrections exclude two imaginary frequencies of 1616i and 1469i cm^{-1}.

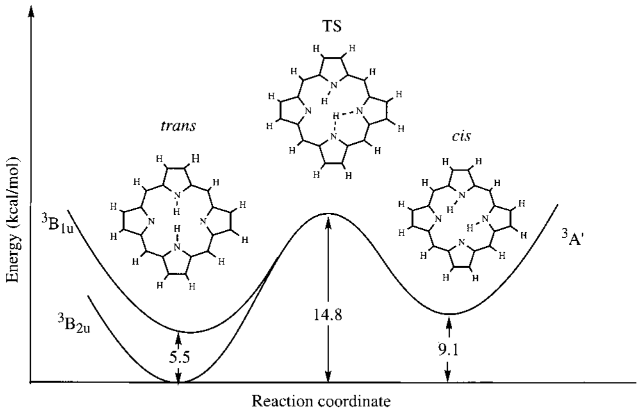

Figure 2. Schematic representation of the potential energy surfaces for the inner-hydrogen transfer reaction.

the molecule equilibrates into the C_s symmetry, the two equivalent $C_\beta-C_\beta$ bonds in the pyrrole rings with inner hydrogens in the cis($^3A_1$) form are distorted from each other by 0.04 Å. The two equivalent $C_\alpha-C_m$ bonds are also shifted by 0.03 Å from each other in the cis($^3A'$) structure (see Figure 1). In comparison with the lowest trans, the major structural changes in the cis−trans isomerization involve increases in the $H-N-C_\alpha$ angles in order to minimize the repulsion between the inner imino hydrogens. The $H-N-C_\alpha$ angle increases from 125° in the trans to 131° in the cis. The N−H bond distances are also slightly longer in the cis.

We now focus on the transition state of the hydrogen atom transfer reaction to show that the tautomerization is capable of proceeding on the triplet PES. The transition search locates the cis−trans transition state at 16.0 kcal/mol above the trans $T_1(^3B_{2u})$ state. This barrier is about 2 kcal/mol higher than the corresponding ground state barrier, at essentially the same level of theory.[7] The observed photoinduced barrier in which excitations are initiated from S_0 followed by an intersystem crossing into the triplet PES, is most likely smaller, since the trans $T_2(^3B_{1u})$ state is 5.8 kcal/mol above the lowest trans $T_1(^3B_{2u})$ state. Note that the T_1-T_2 gap is well within the experimental S_1-T_1 gap of 10.4 kcal/mol.[31] Thus, as the molecule moves into the triplet PES, the trans $T_2(^3B_{1u})$ is initially more populated due to the smaller S_1-T_2 gap. The IHAT from the lowest vibrational level of the trans $T_2(^3B_{1u})$ to the cis($^3A'$) would traverse a barrier of only about 10 kcal/mol. This is consistent with the experimental observation that the IHAT reaction does not occur at the lowest vibrational level of T_1 at a very low temperature.[13] The reverse cis−trans barrier is about 7 kcal/mol. However, the thermodynamic driving force would produce $T_1(^3B_{2u})$ instead of $T_2(^3B_{1u})$ (see Table 1 and Figure 2). Note that the structure of the transition state is more smiliar to the cis than to the trans isomers, as expected from the Hammond postulate. The IHAT migration from the trans $T_1(^3B_{2u})$, especially, involves more structural reorganization than the trans $T_2(^3B_{1u})$. This, again, is consistent with the Hammond postulate.

The two SS structures are found to lie significantly higher in energy than the stepwise transition state (see Table 1). The lowest SS structure, lying at 21.8 kcal/mol above T_1, has two imaginary frequencies of 1616i and 1469i cm^{-1}, with B_{3g} and B_{2u} normal modes, respectively. The second SS($^3B_{2u}$) structure is 24.3 kcal/mol above T_1. This structure has three imaginary frequencies. The transition state search from the distorted geometries along these modes leads back to the SS structure. Thus, DFT calculations suggest that the IHAT reaction occurs via a two-step mechanism involving the cis intermediate on the triplet surface. Finally, comparing the 6-31G(d) results with those of the larger 6-311+G(2d,p) basis set suggests that our DFT calculations are basically converged. The cis−trans relative energy is lowered by only 0.1 kcal/mol upon going to the B3LYP/6-311+G(2d,p) level. Slightly larger differences between the two basis sets are obtained for the barrier and the T_1-T_2 gap.

IV. Summary and Conclusion

The photoinduced hydrogen atom transfer process in free-base porphin has been investigated in detail in order to shed light on the two discordant proposed mechanisms. We found that the IHAT reaction proceeds in a two-step mechanism via a cis intermediate in the triplet state on two PES surfaces. The photoinduced IHAT reaction is predicted to occur from the trans $T_2(^3B_{1u})$ state with the trans−cis isomerization barrier of about 9 kcal/mol. The cis−trans isomerization reaction is predicted to occur primarily on the $^3A'$ PES and produces the lowest triplet trans $T_1(^3B_{2u})$. Thus, the computed results support the proposal that the trans−trans hydrogen transfer occurs in a stepwise fashion through a cis isomer on the triplet PES surface. However, the triplet cis isomer was found to be higher in energy than the corresponding trans isomer where the observed phosphorescence and T_1-S_0 radiationless decay originated.

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Supporting Information Available: A listing of optimized geometries (Cartesian coordinates) for structures in Figure 1.

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