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Multiconfigurational Self-Consistent Field Study of the Excited State Properties of 4-Thiouracil in the Gas Phase

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A comprehensive theoretical study of the vertical singlet and triplet electronic transitions of 4-thiouracil was performed at the multiconfigurational self-consistent field (MCSCF) level of theory. The ground state geometry of the molecule was optimized at the MP2/6-311++G(d,p) level. The MCSCF calculations were performed using the 6-311+G(d) basis set. The active space for the MCSCF calculations consisted of 12 orbitals in which 6 orbitals were the occupied π type while the remaining 6 orbitals were the virtual π^* type. To compute the nπ^* transitions, the two occupied orbitals were replaced with two σ orbitals localized at the thiocarbonyl and carbonyl groups, respectively. Further, MCSCF calculations were also performed with a slightly smaller active space where 10 electrons were distributed in 11 orbitals. The effects of dynamic electron correlation on the MCSCF energies were considered at the second-order multiconfigurational quasi-degenerate perturbation (MCQDPT2) theory. The computed transition energies after the MCQDPT2 correlation were found to be in agreement with the experimental data. The ground and excited state molecular electrostatic potentials and the Mulliken charge distributions in different states were also investigated.

1. Introduction

The determination of the structures and properties of nucleic acid bases and their structural analogues is of continued interest, owing to their widely implicated biological activities. Therefore, it is not surprising that there is a large amount of theoretical and experimental studies on these molecules.[1−5] It is well-known that, in nucleic acid polymers, purine and pyrimidine bases are hydrogen bonded with each other and the specific sequences of hydrogen bonds are the fingerprint of the genetic code.[6] The substitutions of carbonyl groups by thiocarbonyl groups in the bases are expected to alter the helical structure. For example, substitution of 4-thiothymidine in place of thymidine in the Watson−Crick structure yields left-handed double helix structure buildup from the reversed Hoogsteen base pairs.[7] This effect appears due to the fact that sulfur is a heavier and weaker acceptor of the H atom than oxygen. The substitution of sulfur in place of oxygen in molecular systems significantly changes the photophysical properties of the system.[8] For example, the lowest singlet $\pi\pi^*$ and nπ^* states of carbonyl compounds have significantly higher energy than those of the corresponding thiocarbonyl compounds.[9]

The thio analogues of nucleic acid bases have distinctive biological and pharmacological activities.[5,6,10−12] Several thio derivatives have been used as drugs against disease. Thiouracil has been shown as a minor constituent of t-RNA and can be used as anticancer and antithyroid drugs.[6] The 4-thiouracil (4TU) analogues of dUMP are known as good substrates of thymidilate synthase.[13] 4-Thiouracil is also known to possess cytostatic properties and is used as the cross-linking agent in RNA transcriptional regulation.[14] The formation of G tetrads in the guanine rich oligodeoxyribonucleotides can be inhibited by the partial incorporation of the 6-thiocarbonyl analogue of guanine.[15] However, the formation of G.GC triple helixes is not destabilized by the thioguanine.[15] Further, the presence of sulfur in place of oxygen in guanine significantly destabilizes the hydration at the thiocarbonyl group of thioguanine with respect to the guanine.[16]

Different theoretical and experimental investigations have suggested that 4TU exists in the keto-thionic form in the gas phase and in aqueous solution.[5,7,17−21] The existence of a minor tautomeric form of 4TU in the ethanol solution has also been suggested.[17] Rostkowska et al.[7] have performed an IR spectroscopic investigation on thiouracils and their N1 and N3 methyl derivatives in low temperature inert matrixes, and on the basis of their findings, they have suggested that the investigated molecules exist in the keto-thionic tautomeric form. Lamsabhi et al.[18] have used Fourier transform ion cyclotron resonance (FTICR) mass spectrometry and high level ab initio calculation to measure the gas phase proton affinities of thiouracils. It was revealed that thiouracils are somewhat similar moderate bases and protonation takes place at the atom attached to C4 in all thiouracils.[18] Milder and Kliger[22] by performing photolysis of 4-thiouridine (4TUrd), 1,3-dimethyl-4-thiouracil (DMTU), and uracil (U) have shown that quenching of the lowest triplet state of 4TUrd and DMTU by quenchers is due to the electron transfer process.

The multiconfigurational self-consistent field (MCSCF) method has been used to compute electronic transition energies and other properties of nucleic acid bases and related compounds.[23−28] Transition energies obtained after the dynamic electron correlation to MCSCF energies were found to be in good agreement with the corresponding experimental data. In this work, we have used the MCSCF method with an aim to shed some light on the nature of the singlet and triplet transitions of 4TU. The vertical singlet and triplet transition energies, charge distributions, and electrostatic potentials of 4TU in the gas phase computed at the MCSCF level are reported.

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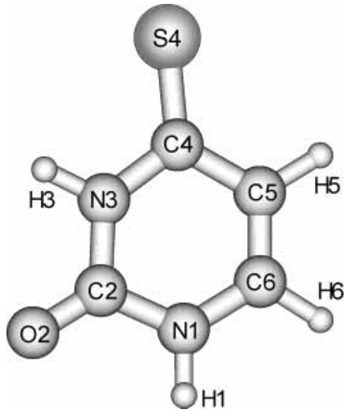


Figure 1. Atomic numbering schemes in 4TU.

TABLE 1: Computed Ground State Rotational Constants (in Megahertz) of 4TU at the MP2/6-311++G(d,p) Level and Ground State Dipole Moments (in Debyes) at the MP2/6-311++G(d,p) and CASSCF/6-311+G(d) Levels

theory		experiment[a]
	dipole moment	
MP2	4.45	4.47
CASSCF	4.41	
	rotational constants	
A	3564.52	
B	1296.64	
C	950.78	

[a] Experimental data in 1,4-dioxane solution (see ref 33).

2. Computational Details

The ground state geometry of 4TU was optimized at the MP2 level using the 6-311++G(d,p) basis set. The ground state optimized geometry was used for the MCSCF calculation to compute the vertical singlet and triplet transition energies. The 6-311+G(d) basis set was used for the MCSCF calculation. The MCSCF active space consisted of the 6π and 6π^* orbitals. Our effort to optimize true MCSCF vertical singlet $\pi\pi^*$ excited states (state with 100% weight) did not converge. Therefore, the vertical singlet first, second, and third $\pi\pi^*$ excited states were obtained with reference weights of 0.9 (0.1 for S_0), 0.7 (0.3 for S_1), and 0.56 (0.22 for S_1 and S_2 each), respectively. To compute the nπ^* transition energies, two π orbitals were replaced with two σ orbitals localized on carbonyl and thiocarbonyl groups. Further, the core orbitals (inactive orbitals) were kept frozen for the nπ^* transition energy calculation. The effects of dynamic correlation on the MCSCF energies were considered using the second-order multiconfigurational quasi-degenerate perturbation (MCQDPT2) theory.[29] The MP2 calculations were performed using the Gaussian 98 program,[30a] while the MCSCF calculations were carried out using the PC GAMESS[30b] version of the GAMESS-US[30c] program. The MOLEKEL program[31] was used for molecular electrostatic potential mapping in the ground and vertical excited states.

3. Results and Discussion

The ground state geometry of 4TU was optimized at the MP2/6-311++G(d,p) level with planar symmetry. The atomic numbering scheme of 4TU is displayed in Figure 1. The ground state dipole moment and rotational constants computed at the MP2/6-311++G(d,p) level are shown in Table 1. It should be noted that in the crystallographic study the geometry of 4TU was revealed to be planar.[32] Further, theoretical calculations at the different levels of theory have also shown that the ground state geometry of 4TU is planar.[5,17−19] In addition, IR matrix isolation and UV−vis spectroscopic studies on 4TU have shown that it exists in the keto-thione form.[5,7,20,21] These findings were also supported by the theoretical calculations at the different levels of theory both in the gas phase and in aqueous solution.[5,17−19] The computed ground state dipole moment of 4TU at the MP2/6-311++G(d,p) level was found to be 4.45 D, while at the CASSCF/6-31+G(d) level it was found to be 4.41 D. The experimental measurement of the dipole moment of 4TU was performed in 1,4-dioxane solution and yielded 4.47 D.[33] Therefore, the computed dipole moment is in excellent agreement with the experimental data. To the best of our knowledge, information about the experimental rotational constants of 4TU is not yet available, and therefore, we are unable to compare our computed data. However, we believe that our data should provide reliable information regarding the rotational constants of the molecule.

Computed transition energies of 4TU are shown in Table 2 along with the corresponding experimental data for 4TU and 4-thiouridine (4TUrd) obtained in water and in acetonitrile.[21] It should be noted that in the case of the nπ^* transitions the transition energies for the lowest energy transitions only are given. The MCQDPT2 method predicted the lower three vertical singlet $\pi\pi^*$ transitions at 3.9, 4.53, and 4.79 eV for 4TU. The absorption, magnetic circular dichroism (MCD), and circular dichroism (CD) spectra of 4T and 4TUrd in water and in acetonitrile have shown that the lower two singlet $\pi\pi^*$ transition energies are generally in the 3.8 and 4.7 eV region (Table 2).[21] Therefore, the computed first two transition energies are in good agreement with the corresponding experimental data. The absorption measurement of 4TU and 4TUrd suggests that the third transition would be near 5.1 eV in the water solution and near 5.0 eV in the acetonitrile solution.[21] The computed third transition near 4.8 eV can also be regarded to be in good agreement with the experimental data. Here, it should be noted that the computed transition energies correspond to the gas phase of the molecule. Therefore, it is expected that the inclusion of the effect of the solvent environment for the computed transition energies would yield good agreement with the experimental data.

Igarashi-Yamamoto et al.[21] have reported the existence of a weak CD band near 3.1 eV (400 nm) in 4TUrd in an acetonitrile solution. This transition was assigned as being due to the nπ^* transition. Our computed vertical singlet nπ^* transition at 2.82 eV at the MCQDPT2 level can be explained in terms of the experimental nπ^* transition. Among triplet transitions, the first vertical triplet $\pi\pi^*$ state is ∼0.1 eV lower in energy than the first triplet nπ^* state. The lowest singlet vertical nπ^* state is only ∼0.07 eV higher in energy than the lowest triplet nπ^* state at the MCQDPT2 level (Table 2). Further, both nπ^* transitions (singlet and triplet) are characterized by the excitation of the thiocarbonyl group of the molecule. There are contradictory results regarding the nature of the lowest triplet state of 4TU. Salet et al.[34] have suggested that for 4TUrd the lowest triplet state is of the nπ^* type. On the other hand, Taherian and Maki[35] on the basis of an optically detected magnetic resonance (ODMR) study on 1-methyl-2-thiouracil, 1-methyl-4-thiouracil, and 1-methyl-2,4-dithiouracil have suggested that the lowest triplet state of thiouracils is of the $\pi\pi^*$ type. Milder and Kliger[22] have performed a laser photolysis study on uracil, 4-thiouridine, and 1,3-dimethyl-4-thiouracil in different solvents along with intermediate neglect of differential overlap/spectroscopic parametrization (INDO/S) calculations to study the triplet states of these molecules. These investigations have also suggested

TABLE 2: Computed and Experimental Transition Energies (Δ*E*, in Electronvolts) and Dipole Moments (*μ*, in Debyes) of 4TU

				experimental ΔE^a									
				4TU				4TUrd					
	MCQDPT2	CASSCF		water		ACN		water			ACN		
transition	ΔE	ΔE	μ^b	abs	MCD	abs	MCD	abs	CD	MCD	abs	CD	MCD
$S_1(\pi\pi^*)$	3.90	4.79	5.75	3.78	3.84	3.79	3.81	3.75	3.59	3.78	3.75	3.72	3.72
$S_2(\pi\pi^*)$	4.53	5.46	6.93		4.68		4.68		4.61	4.73		4.59	4.64
$S_3(\pi\pi^*)$	4.79	6.17	4.64	5.08	5.32	5.02		5.08	5.34		5.06	5.32	5.39
$S_1(n\pi^*)$	2.82	3.09	3.24									3.10	
$T_1(\pi\pi^*)$	2.64	2.75	3.11					2.29					
$T_2(\pi\pi^*)$	3.16	4.38	3.74					3.03					
$T_1(n\pi^*)$	2.75	2.95	3.29										

[a] ACN, acetonitrile; 4TUrd, 4-thiouridine. For experimental data, see ref 21. In case of triplet transitions, see ref 22. [b] The ground state dipole moment is 4.41 D.

TABLE 3: Orbital Occupation Numbers of 4-Thiouracil in the Ground and Vertical Singlet and Triplet Excited States Obtained at the MCSCF/6-311+G(d) Level

state	$1\pi/\sigma$	$2\pi/\sigma$	3π	4π	5π	6π	7π	8π	9π	10π	11π	12π
S_0	2.000	1.985	1.977	1.957	1.942	1.914	0.096	0.009	0.061	0.004	0.046	0.009
$S_1(\pi\pi^*)$	2.000	1.979	1.954	1.950	1.905	0.558	1.469	0.008	0.093	0.020	0.054	0.010
$S_2(\pi\pi^*)$	2.000	1.969	1.943	1.914	1.348	1.571	1.020	0.009	0.123	0.015	0.077	0.010
$S_3(\pi\pi^*)$	2.000	1.974	1.920	1.929	1.683	1.252	0.615	0.010	0.507	0.028	0.010	0.074
$S_1(n\pi^*)$	1.999	1.000	1.983	1.959	1.918	1.993	1.000	0.085	0.044	0.010	0.007	0.003
$T_1(\pi\pi^*)$	2.000	1.985	1.977	1.957	1.901	1.033	0.971	0.010	0.099	0.004	0.052	0.010
$T_2(\pi\pi^*)$	2.000	1.980	1.973	1.944	1.240	1.710	0.770	0.010	0.300	0.004	0.011	0.058
$T_1(n\pi^*)$	1.999	1.000	1.983	1.959	1.919	1.992	1.000	0.010	0.084	0.003	0.043	0.006

that the lowest triplet state of thiouracils is of the ππ* type. Thus, our computed result showing that the $T_1(\pi\pi^*)$ state is ~0.11 eV lower in energy than the corresponding nπ* state (Table 2) supports the experimental findings of Taherian and Maki[35] and Milder and Kliger[22] that the lowest triplet state of 4TU is of the ππ* type. The computed triplet ππ* transition energies at 2.64 and 3.16 eV can be explained in terms of the experimental transition energies near 2.29 and 3.0 eV of 4TUrd in water solution.[22] It should be noted that in the experiment a triplet ππ* transition was also obtained near 1.70 eV.[22] However, surprisingly, our calculated results do not support an existence of a triplet ππ* transition in the 1.7 eV region.

The orbital occupation numbers of 4TU in the ground and excited states are shown in Table 3. It is clear that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the active space are the most important. However, for the second and third singlet and second triplet ππ* states, the HOMO−1 and LUMO+2 are also involved in excitations. The nature of the HOMO−1, HOMO, LUMO, and LUMO+2 is shown in Figure 2. It is clear from Figure 2 that the HOMO−1 and HOMO are dominated by the π-type bonding orbital of the C5−C6 bond while the LUMO and LUMO+2 are dominated by the antibonding π-type orbital of the C5−C6 bond. In going from the ground state to excited states, the dipole moments of the singlet ππ* excited states are increased, while those in the singlet nπ* and triplet states are decreased (Table 2). Among the singlet ππ* states, the second singlet state has the highest dipole moment, while in the third state, only a slight increase is predicted. Interestingly, the dipole moment of the T1(ππ*) state is slightly lower than that of the T1(nπ*) state (Table 2). Further, it should be mentioned that the occupation number of the 1π orbital of the active space is found to be nearly 2, suggesting that this orbital was almost doubly occupied throughout the calculations.

Therefore, the MCSCF calculations were also performed considering a smaller active space with 11 orbitals and 10 electrons obtained by deleting the 1π/1σ orbitals of the larger active space (12 orbitals and 12 electrons). Computed transition energies from the smaller active space are presented in Table 4. It is evident from the comparison of data shown in Tables 2 and 4 that the CASSCF vertical transition energies are stabilized even in a smaller active space. The computed dipole moments for the ππ* transitions also do not show significant change in

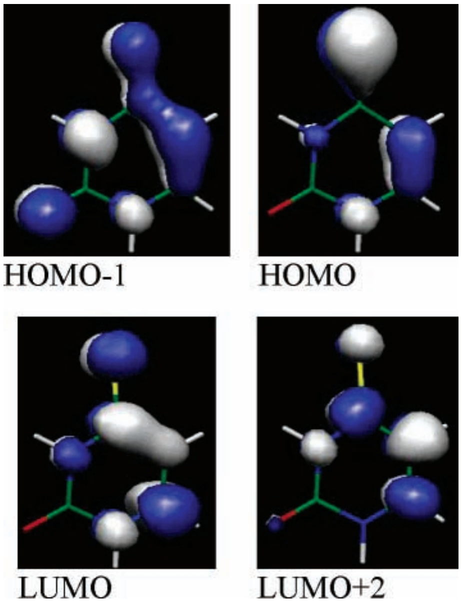

HOMO-1 HOMO
LUMO LUMO+2

Figure 2. The HOMO−1, HOMO, LUMO, and LUMO+2 of 4TU in the ground state.

TABLE 4: Computed Transition Energies (Δ*E*, in Electronvolts) and Dipole Moments (*μ*, in Debyes) of 4TU with a Smaller Active Space (10 Electrons Occupying 11 Orbitals)

	MCQDPT2	CASSCF			MCQDPT2	CASSCF	
transition	ΔE	ΔE	μ^a	transition	ΔE	ΔE	μ^a
$S_1(\pi\pi^*)$	3.88	4.80	5.75	$T_1(\pi\pi^*)$	2.63	2.76	3.11
$S_2(\pi\pi^*)$	4.44	5.46	6.90	$T_2(\pi\pi^*)$	3.00	4.39	3.74
$S_3(\pi\pi^*)$	4.78	6.17	4.64	$T_1(n\pi^*)$	2.65	2.96	3.25
$S_1(n\pi^*)$	2.73	3.11	3.14				

[a] The ground state dipole moment is 4.41 D.

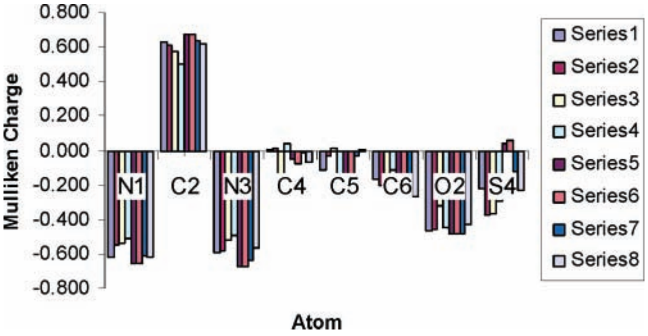
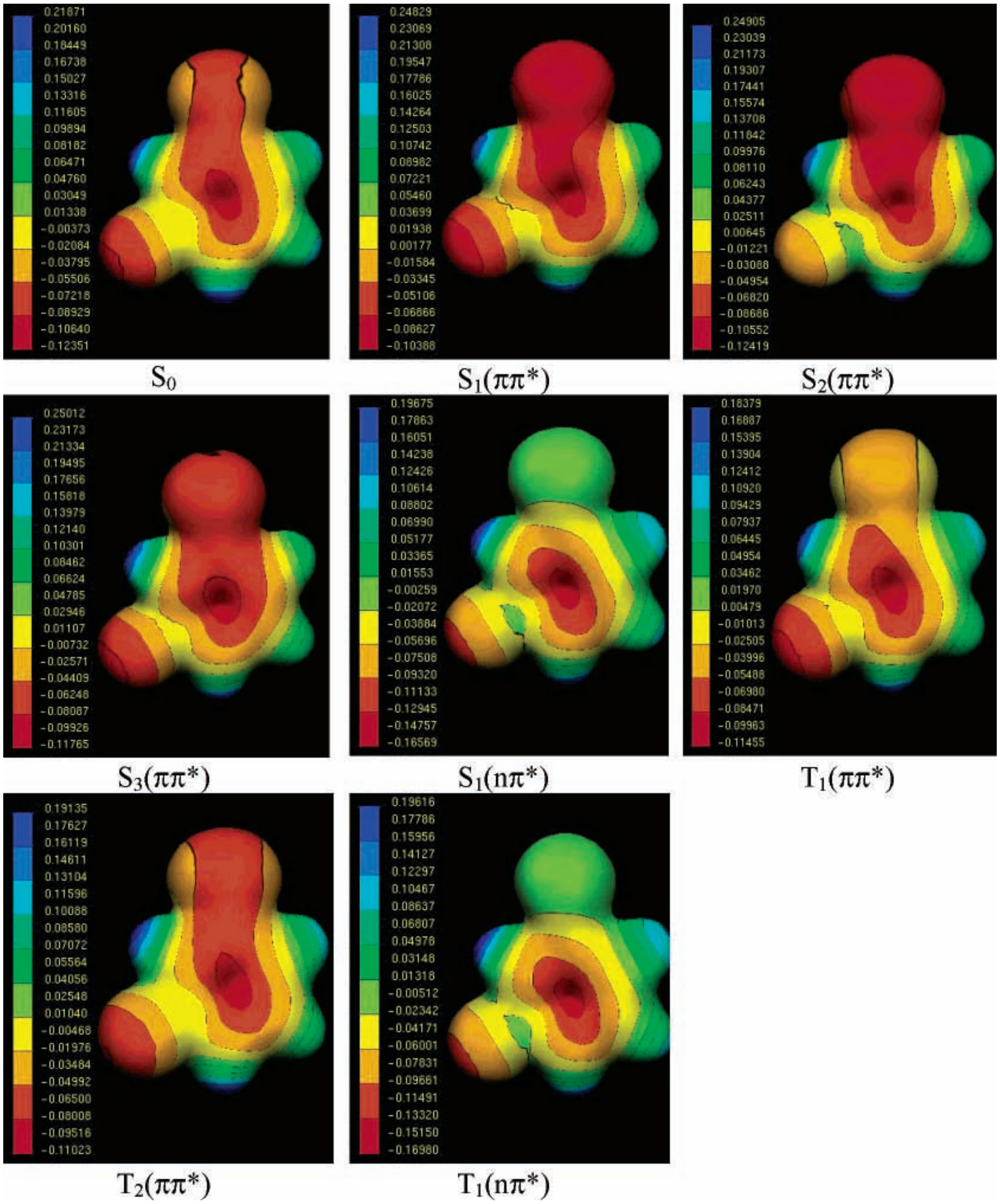


Figure 3. Bar diagram of the Mulliken charges in the ground and vertical excited states of 4TU at different atomic sites (except hydrogen atoms) computed at the MCSCF/6-31+G(d) level. Series 1−8 represent the S_0, $S_1(\pi\pi^*)$, $S_2(\pi\pi^*)$, $S_3(\pi\pi^*)$, $S_1(n\pi^*)$, $T_1(n\pi^*)$, $T_1(\pi\pi^*)$, and $T_2(\pi\pi^*)$ states, respectively.

the smaller active space. However, for the nπ^* transitions, the dipole moment of the singlet and triplet states is decreased by ~0.1 and ~0.04 D, respectively, in the smaller active space. The inclusion of dynamic electron correlation at the MCQDPT2 level shows that the transition energies of the singlet first and third and triplet first $\pi\pi^*$ states do not change significantly in the smaller active space; however, the transition energies of the second singlet and triplet $\pi\pi^*$ states and those of the nπ^* states show noticeable change. This would yield the lowest triplet $\pi\pi^*$ state being only 0.02 eV lower in energy than the corresponding nπ^* state. Thus, smaller active space calculation does not change the nature of the lowest triplet state; however, the energy difference between the $T_1(\pi\pi^*)$ and $T_1(n\pi^*)$ states is significantly decreased. It should be noted that the smaller active spaces for the nπ^* transition energy calculations were obtained by deleting the 1σ orbital of the larger active space (Table 3). However, selection of a smaller active space for the nπ^* states might not be justified, since the occupation number for 1σ is 1.999, which might be responsible for the energy change under dynamic electron correlation using the MCQDPT2 method.



S_0 $S_1(\pi\pi^*)$ $S_2(\pi\pi^*)$

$S_3(\pi\pi^*)$ $S_1(n\pi^*)$ $T_1(\pi\pi^*)$

$T_2(\pi\pi^*)$ $T_1(n\pi^*)$

Figure 4. Molecular electrostatic potential maps of 4-thiouracil in different vertical states obtained at the MCSCF/6-31+G(d) level.

Further, since the computed accuracy of the applied method in this paper is generally ~0.1−0.2 eV, one may question the predicted order of the lowest triplet $\pi\pi^*$ and $n\pi^*$ states on the basis of the energy difference between these two states. It can be addressed by the additional calculation with a larger active space. However, the unavailability of more occupied π orbitals and the fact that other virtual π^* orbitals are largely Rydberg contaminated do not give the flexibility of additional calculation. It should be mentioned that good orbitals in the active space are necessary for reliable results. Therefore, on the basis of the present theoretical calculation, it is highly likely that the lowest triplet $\pi\pi^*$ state would be lower in energy than the lowest triplet $n\pi^*$ state. Further, since the energy difference between the lowest triplet $\pi\pi^*$ and $n\pi^*$ states is increased from 0.02 to 0.11 eV in going from 11 orbitals to 12 orbitals in the active space, we believe that the use of a better basis set that is preferably correlation consistent with highly diffuse function may further increase the gap between the two states.

A bar diagram of Mulliken charges at the atomic sites of the heavy atoms of 4TU is shown in Figure 3. In this figure, series 1−8 represent the S_0, $S_1(\pi\pi^*)$, $S_2(\pi\pi^*)$, $S_3(\pi\pi^*)$, $S_1(n\pi^*)$, $T_1(n\pi^*)$, $T_1(\pi\pi^*)$, and $T_2(\pi\pi^*)$ states, respectively. As expected, the Mulliken charge distributions are generally changed in going from the ground state to different excited states of 4TU (Figure 3). In general, the charge at the thiocarbonyl group is significantly decreased in the lowest vertical singlet and triplet $n\pi^*$ states as compared to that in the ground state. In going from the ground state to the $S_1(\pi\pi^*)$ excited state, the N1 and C5 atoms lose (0.075 and 0.083 au, respectively) and the S4 atom gains (0.154 au) a significant amount of electronic density. In the $S_2(\pi\pi^*)$ excited state, significant rearrangement of the Mulliken charge is revealed as compared to the ground state. The N1, N3, C5, and O2 atoms lose (0.076, 0.064, 0.132, and 0.143 au, respectively) and the C2, C4, C6, and S4 atoms gain (0.055, 0.180, 0.073, and 0.140 au, respectively) a significant amount of electron density in this state. In the $S_3(\pi\pi^*)$ excited state, the N1, N3, and C6 atoms lose (0.106, 0.095, and 0.055 au, respectively) and the C2, C5, and S4 atoms gain (0.127, 0.156, and 0.070 au, respectively) a significant amount of electronic density as compared to the corresponding ground state values. In the $S_1(n\pi^*)$ excited state, all heavy atoms except the C2 atom gain electronic density at the expense of charge at the S4 atom in comparison to that in the ground state. In this state, the S4 atom loses 0.262 au of electronic charge. The charge distribution in the $T_1(n\pi^*)$ state is similar to that in the $S_1(n\pi^*)$ excited state. Therefore, in going from the ground state to the $T_1(n\pi^*)$ state, all heavy atoms except the C2 atom gain electronic charge at the expense of charge at the S4 atom. The S4 atom loses 0.285 au of electronic charge in this state. In the lowest triplet $\pi\pi^*$ excited state ($T_1(\pi\pi^*)$), generally a significant change in the charge distribution is not revealed as compared to that in the ground state. The C5 and S4 atoms lose (0.085 and 0.097 au, respectively) and the N3 and C6 atoms gain (0.047 and 0.069 au, respectively) electron charge in this state. In the $T_2(\pi\pi^*)$ state, the C5 atom loses (0.118 au) and the C4 and C6 atoms gain (0.073 and 0.098 au, respectively) a significant amount of Mulliken charge as compared to the corresponding ground state values (Figure 3). It should be noted that in the above discussion other atoms also show change in charge distributions but their contribution is comparatively smaller.

The molecular electrostatic potentials (MEPs) mapped onto the electron density of 4TU in the ground and different excited states are shown in Figure 4. It is evident from Figure 4 that, as expected, the MEP features are generally modified appreciably in going from the ground state to different excited states. In the ground state, the minimum electrostatic potential (with a red color) is located at the O2 site and near the center of the ring, while, in the $S_1(\pi\pi^*)$ excited state, the minimum electrostatic potential region is more extended toward the S4 site. In the $S_2(\pi\pi^*)$ excited state, the MEP features are generally similar to those in the $S_1(\pi\pi^*)$ state except that the O2 site in the $S_2(\pi\pi^*)$ excited state has a higher potential value. The MEP features of the $S_3(\pi\pi^*)$ excited state are generally similar to those in the ground state. The MEP features of the $S_1(n\pi^*)$ and $T_1(n\pi^*)$ excited states are generally similar. The minimum electrostatic potential is located at the O2 site and near the center of the ring. Further, the S4 region is characterized by the positive electrostatic potential (Figure 4). The prediction of the positive electrostatic potential near the S4 region in the $S_1(n\pi^*)$ and $T_1(n\pi^*)$ excited states, as expected, is in accordance with the nature of state which is characterized by the excitation of the thiocarbonyl group. The MEP features of the $T_1(\pi\pi^*)$ and $T_2(\pi\pi^*)$ states are generally similar and close to those in the ground state except for the fact that the S4 region of the $T_1(\pi\pi^*)$ state is characterized by a comparatively more positive potential.

4. Conclusions

The MCQDPT2 computed transition energies of 4TU are found to be in good agreement with the experimental data. It is expected that the inclusion of the solvation effect in transition energies would increase the agreement with the experimental data. Our theoretical data also indicate that the lowest triplet state of 4TU would be of the $\pi\pi^*$ type. As expected, the Mulliken charge distributions and MEP maps are significantly modified in going from the ground state to different excited states. Further, as compared to the ground state, significant charge transfer from the sulfur atom to the heavy atoms of the ring is revealed in the vertical singlet and triplet $n\pi^*$ states.

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