considering the triplet structures of C_3H_2, found that the lowest was propargylene (~**19**), followed by propadienylidene (~**20**), propenediylidene (~**22**, ~**26**), cyclopropenylidene (~**21**, ~**25**), and cyclopropyne (~**23**, ~**24**). Our calculations at the minimal level suggest that the lowest triplet structures are **19–25** and that these were then optimized at the UMP2(DZP) level, and results are given in Table III.

These calculations show that the Si insertion structure **19** (^3A) is the lowest, with the structure **20** ($^3A_2$) lying very close in energy. As shown in Tables III and IV, the energy difference between them is 0.5 and 2.5 kcal/mol at the UMP2(DZP) and UMP2-(TZ2P) levels, respectively. **19** does not have the odd W shaped structure proposed by Hehre et al. for C_3H_2 but seems to be an entirely reasonable structure for the Si-containing molecule. The structure for **20** is again acceptable and favorable because it can be drawn with a C=Si bond.

If one considers a C_{2v} approach of Si(^{3}P) to C_2H_2, then in analogy with SiC_2H_4 there will be $^3B_1$, $^3B_2$, and $^3A_2$, which is found again to have one imaginary frequency. On distortion the low-lying structure $^3A''$ **22** is found which can be formed from Si(^{3}P) and C_2H_2 without a barrier. In this case the $^3B_1$ is not a minimum, but the optimized structure **25**, ^3B, is a minimum.

Structure **23** is considerably lower in energy than structure **24**, corresponding again to Si's preference for divalency.

We believe that structures **19–25** include the lowest triplet structure of SiC_2H_2. The lowest singlet is the silacyclopropenylidene structure, as determined by Frenking et al. from an examination of 15 isomers. We optimized this structure, and it is shown in Figure 5 as structure **35**; its energy is reported in Table III from which it is seen that it lies 47 kcal/mol below the lowest triplet isomers **19** and **20**.

V. Conclusion

In this paper we have studied the triplet isomers of SiC_2H_4 and SiC_2H_2. Our results may be summarized as follows.

(i) The lowest energy structure of SiC_2H_4 is the $^3A_2$ structure **1a** of Figure 1. It may be formed from Si (^{3}P) + C_2H_4 without a barrier. There are two other structures, **2** and **3**, which lie close in energy to **1a**. Structure **1a** lies 37.0 kcal/mol above the global minimum singlet structure **14** (Figure 1).

(ii) The lowest energy structure of SiC_2H_2 is the ^3A structure **19** with the $^3A_2$ structure **20** having almost the same energy, both lying 48 kcal/mol above the global minimum singlet structure **35**. The structure **22** which is bound with respect to Si(^{3}P) + C_2H_2 may be formed without a barrier. Note that this is not a ring structure (unlike the $^3A_2$ structure **1a** in Si(^{3}P) + C_2H_4).

Finally therefore, the kinetic experiments of Basu and Husain may be explained: for Si(^{3}P) + C_2H_4, the low-lying structure **1a** is formed without a barrier; for Si(^{3}P) + C_2H_2, the structure **22** of may be formed without a barrier, although in this case it is not the lowest triplet structure.

Registry No. Si, 7440-21-3; C_2H_4, 74-85-1; C_2H_2, 74-86-2.

Tautomerism of 2- and 4-Thiouracil. Ab Initio Theoretical Study

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Abstract: Ab initio quantum mechanical studies on tautomerism are extended to the 2-thiouracil and 4-thiouracil molecules. We considered the protomeric tautomerism in vacuum and conclude that for both species the oxo–thione forms should prevail in full agreement with recent experimental matrix isolation studies. Surprisingly, the next most stable structure appears to be the hydroxy–mercapto form. The relevance of the relative stability order of 2-thiouracil and 4-thiouracil to the tautomerism of various derivatives is discussed. Major features of the vibrational spectra of various tautomeric forms are presented and compared with the experiment.

The protomeric tautomerism of heterocycles, including biologically important pyrimidines and purines, has attracted considerable attention for almost half a century.[1] Both experimental[1,2] and theoretical[2,3] efforts were directed toward determination of numerous physicochemical properties of possible tautomeric forms. It has been realized that the relative population of these forms strongly depends on the environment.[3,4] In particular, the form dominating in the gas phase or in the nonpolar solvents may completely disappear in the crystalline state or in the polar solvents and may be replaced by another tautomeric form. Such a dramatic shift in concentrations will certainly affect the metabolism of heterocycles in biological systems. In the context of our theoretical studies on the tautomerization phenomenon, we have recently directed our interest toward the tautomerism of nucleobase thio derivatives that contain sulfur atoms in the positions of the exocyclic oxygen atoms. Their protomeric tautomerism is somewhat different than that of the parent bases.[5] The thiated nucleobases appear naturally in various biological materials and are important agents for numerous metabolic processes. Many of them have been characterized in tRNAs,[6] e.g. 4-thiouridine in prokaryotic tRNAs, 2-thiouridine in Drosophila $tRNA^{Glu}$,[7] and 2-thiocytidine in prokaryotic tRNA.[6] Also, the corresponding thio derivatives of the purinic base have been identified.[8] It is reasonable to assume that in some nucleic acids the sulfur substitution affects the conformations of a helix

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through the changes in the hydrogen bondings and the stacking interactions. As a result, one may expect modifications of the recognition patterns exerted by enzymes involved in the nucleic acid metabolism.

In the past few years, considerable attention has been paid to 2-thiouracil and 4-thiouracil. Although very similar in structure, these compounds have different biological activities. It was established that 2-thiouracil acts as a carcinogen, neoplastigen, tumorigen, and teratogen agent.[9] Also, the antithyroid activity of this compound and its 6-alkyl derivatives (e.g. 6-propyl-2-thiouracil, PTU) is well documented.[10] Moreover, the 2-thiouracil moiety, which involves the thioamide N(1)–C(2)S–N(3) bond sequence, occurs in the 5-member ring of methimazole, which is a very potent antithyroid drug.[10] The antithyroid activity of 2-thiouracil is probably related to the redox processes affecting the metabolism of the enzyme thyroxine. If so, the 2-thiouracil would rather be oxidized than reduced, as it has been, indeed, argued in the electrochemical studies.[10-13] Worth mentioning is a recent extension of the electrochemical study of 2-thiouracil on its interaction with transition-metal ions/electrodes.[14]

Both 2-thiouracil and 4-thiouracil possess interesting functions as agents in chemical synthesis of modified nucleosides. Studies have been undertaken in order to understand the mechanism of biological transformations of nucleic acid components,[15-18] and it has been shown that the chemical activities of 2-thiouracil and 4-thiouracil toward some thiating agents are different (e.g. toward the Lawesson reagent). Thus, one can infer that the discrimination between 2- and 4-thiouraciles by biological systems[19] can be understood at the chemical level.

The knowledge of physicochemical properties of the isolated 2-thiouracil and 4-thiouracil molecules is an essential prerequisite in understanding their interaction in various chemical and biological environments. Several experimental and theoretical attempts have been undertaken in the past toward this goal. The dipole moment, which is needed to account for the molecular interactions with environments of different polarities, was measured several years ago.[20] It was also calculated by means of theoretical semiempirical methods.[21] Some rigid conformations that appear in the solid, liquid, and gas phases can be identified with use of the crystal structures of the 2-thio- and 4-thiouracil moieties.[22,23] Such conformations may be crucial in understanding the drug–receptor interactions involving thiobases. Also, the crystal data will help to identify which tautomeric forms of 2-thiouracil are present in some cyclonucleosides. In these compounds the sulfur atom of thiouracil forms a bridge between the pyrimidine C(2) atom and the ribose C(5′) or C(2′) atoms. The ability of thiouracils to adopt either a cationic or an anionic form (through protonation or deprotonation) can be characterized by means of the ionization constants, pK_a. The available data[25] suggest that the thiouracils are stronger acids than uracils. The identification of the thiouracil moieties involved in the nucleic acids can be accomplished by means of the spectral methods, e.g. UV[26-28] and ESCA,[29,30] the infrared and Raman,[27,31-37] and the ^1H NMR spectroscopies.[41]

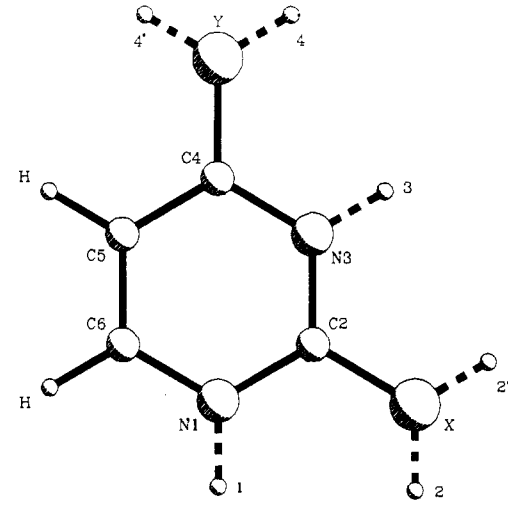

Figure 1. The accessible positions for two hydrogen atoms during tautomerization in 2-thiouracil (X = S, Y = O) and 4-thiouracil (X = O, Y = S).

Until very recently the molecular structures of thiouracils were ambiguous to some extent. It is somewhat surprising that in past IR/NMR studies the rare hydroxy–thiol structures were commonly assumed for the isolated thiouracil molecule.[38] The same structures were propagated in widely distributed reference books.[39-42] The recent IR and Raman studies in gas and solid phases have revealed that 2-thiouracil and 4-thiouracil exist in the oxo–thione forms.[34] The pioneering efforts of Szczepaniak's group[27] using the low-temperature matrix-isolation techniques definitely confirmed these observations beyond any doubt. From the very recent ^1H NMR in DMSO-d_6 measurements[16] it can also be concluded that 2-thiouracil exists in the oxo–thione form.

There is, however, a possibility that the rare tautomers of thiouraciles are simply not observed due to their very low concentration and due to the limited resolution of spectrometers used in experimental studies. Theoretical calculations based on the quantum mechanical principles may certainly help to resolve the question of the relative stability of various tautomeric forms of thiouracils and to predict the relative gas-phase abundance of those forms. This is the approach taken in the present studies.

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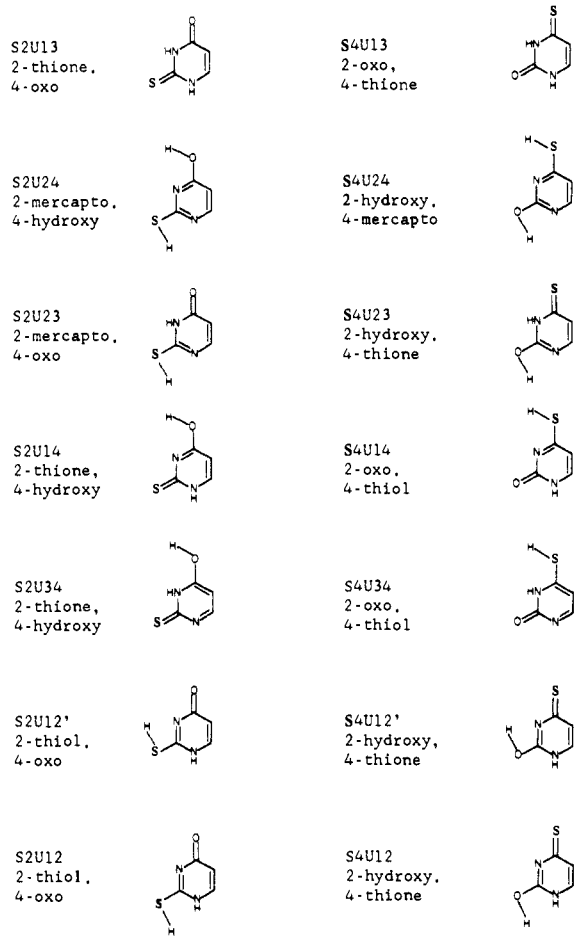

Figure 2. The tautomers of 2-thiouracil and 4-thiouracil considered in the present paper. The notation S*n*U*xy* stands for *n*-thioUracil with two protons located at *x* and *y* positions of the pyrimidine ring.

There have been very few theoretical calculations concerning this subject. Because of the considerable size of thiouracils by quantum mechanical standards, only semiempirical[21,43,44] or quasi-ab initio[45] methods have been applied so far. The relative stability of various tautomers was predicted with a similar dispersion as one may find in the experimental studies. In the present work we re-visited the problem of the molecular structure and tautomerism of 2- and 4-thiouracil at advanced levels of theory. We apply the ab initio one-particle model (Hartree–Fock) for electronic structure calculations and correct it for the electron correlation effects in the final evaluation of the total molecular energies. The nuclear zero-point motion is also accounted for. The vibrational analysis is performed assuming the harmonic approximation at the SCF/3-21G* level by means of analytical derivatives of the total molecular energy. A similar procedure was applied before to study the tautomeric equilibria of cytosine,[46] 5-fluorocytosine,[47] uracil and 5-fluorouracil,[48] and 5-methylcytosine.[49]

Results and Discussion

We consider here several tautomeric forms of 2-thiouracil and 4-thiouracil. The forms differ by the positions of two protons either in the vicinity of ring nitrogen atoms or exocyclic sulfur/oxygen atoms (see Figures 1 and 2).

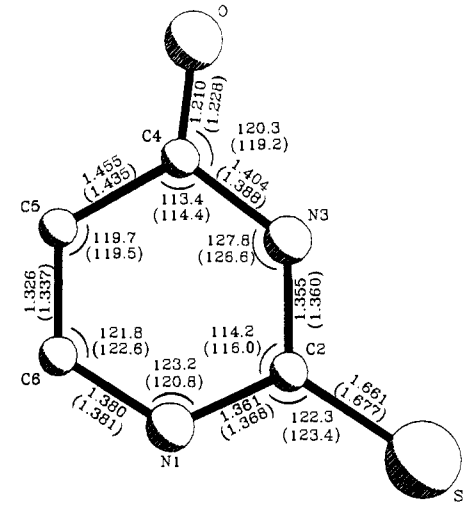

Figure 3. The optimized SCF/3-21G* geometry of 2-thiouracil. The crystal data of 2-thiouridine[22] are given in parentheses.

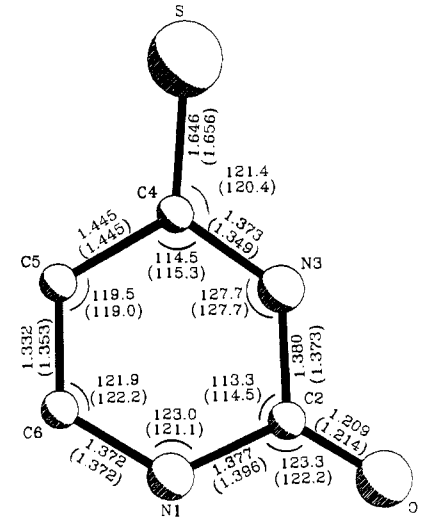

Figure 4. The optimized SCF/3-21G* geometry of 4-thiouracil. The crystal data of 4-thiouridine[23] are given in parentheses.

The optimization of the molecular geometry is an essential step in the theoretical prediction of the relative stability of various tautomeric forms,[3] and we performed this with the standard 3-21G* basis set at the SCF level.[50] The calculated geometries have been compared with the crystal data of the respective nucleosides, i.e. 2-thiouridine[22] and 4-thiouridine.[23] The agreement between theory and experiment is fairly good (see Figures 3 and 4), and the discrepancies are of the order of experimental accuracy. Small discrepancies are unavoidable because the theoretical calculation suffered from several drawbacks, e.g. the crystal forces were not included, a limited, not saturated basis set was used, the electron correlation effects were omitted.

In order to predict the relative stability of various tautomeric forms the SCF/3-21G* structure optimizations were followed by a single-point SCF+MBPT(2) (SCF energy plus the second-order correlation correction based on the many-body perturbation theory) energy calculation with the standard 6-31G** basis set. This basis set comprises the polarization functions on both hydrogens and heavier atoms. We have already argued[46-49] that the hydrogen polarization functions are especially essential for quantitative prediction of the protomeric tautomerism. The preliminary selection of tautomeric forms was performed on the basis of the total energies obtained with the 3-21G* basis set. The oxo–thione tautomers for both 2- and 4-thiouracil were clearly

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Table I. SCF, MBPT(2), and ZPE Energies (hartrees) for 2-Thiouracil

tautomer	basis set	SCF	SCF+MBPT(2)	ZPE	total[a]	rel energies, kJ mol^{-1}
S2U13	3-21G*	−731.375 126		0.092 967		
	6-31G**	−735.111 661	−736.245 344		−736.160 744	0.0
						(0.0)[b]
S2U24	3-21G*	−731.334 168		0.087 378		
	6-31G**	−735.092 341	−736.229 964		−736.150 450	27.0
						(45.6)[b]
S2U23	3-21G*	−731.339 076		0.088 324		
	6-31G**	−735.090 583	−736.227 348		−736.146 973	36.2
						(43.9)[b]
S2U14	3-21G*	−731.343 189		0.091 537		
	6-31G**	−735.089 063	−736.225 028		−736.141 729	49.9
						(50.2)[b]
S2U34	3-21G*	−731.321 039		0.090 020		
	6-31G**	−735.067 349	−736.214 394		−736.132 476	74.2
S2U12′	3-21G*	−731.323 728		0.087 985		
S2U12	3-21G*	−731.317 673		0.087 663		

[a] Total energy = SCF + MBPT(2) + η*ZPE; η = 0.91.[46] [b] Uracil with the DZP basis set, ref 48 and present calculations.

Table II. SCF, MBPT(2), and ZPE Energies (hartrees) for 4-Thiouracil

tautomer	basis set	SCF	SCF+MBPT(2)	ZPE	total[a]	rel energies, kJ mol^{-1}
S4U13	3-21G*	−731.377 057		0.092 952		
	6-31G**	−735.114 132	−736.248 631		−736.164 045	0.0
						(0.0)[b]
S4U24	3-21G*	−731.333 132		0.087 399		
		−735.092 104	−736.229 068		−736.149 535	38.1
						(45.6)[b]
S4U23	3-21G*	−731.351 988		0.091 691		
	6-31G**	−735.097 275	−736.231 409		−736.147 970	42.2
						(43.9)[b]
S4U14	3-21G*	−731.337 733		0.088 472		
	6-31G**	−735.089 156	−736.225 741		−736.145 230	49.4
						(50.2)[b]
S4U12′	3-21G*	−731.334 960		0.091 281		
S4U34	3-21G*	−731.327 240		0.087 661		

[a] See footnote *a* to the Table I. [b] Uracil with the DZP basis set, ref 48 and present calculations.

the most stable ones. However, the next form on the stability scale was not so obvious to predict and calculations on several possible structures were needed to sort out this question. We present various contributions to the tautomers relative stability for 2-thiouracil and 4-thiouracil in Tables I and II, respectively. For comparison we add the relative total energies of four tautomeric forms of uracil (parent compound). Qualitatively, the results for thiouracils are also visualized in Figure 5. One can see that the relative stability order obtained at the SCF/3-21G* level is erroneous. In general, the SCF level of theory, even with a more extended double-ζ basis set augmented with polarization functions, does not yet ensure the correct stability order. As our results for the 2-mercapto, 4-hydroxy tautomer of 4-thiouracil indicate, it is essential to account for both the electron correlation effects and the zero-point vibration contributions in order to correctly position this form on the bottom of the relative energy scale (see Figure 5). Qualitatively, the extraordinary stability of the hydroxy–mercapto form just next to the oxo–thione tautomer can be understood as a tendency of the pyrimidine ring to adopt the aromatic structure. The precise theoretical description of the ring aromaticity certainly mandates the calculation of the electron correlation effects. Our present approach to account for these effects rests on the second-order perturbation procedure. Studies on higher order correlation effects using the coupled cluster method and the first-order correlation orbitals[47] will be conducted in the near future.

At the presently applied level of theory we conclude that the substitution of exocyclic oxygen by sulfur atoms in thiouraciles makes the tautomerization process easier than in unsubstituted uracil. The energy splitting between the normal thione–oxo form and the closest rare tautomer can be estimated to be about 23 kJ mol^{-1}. In uracil the respective value is 44 kJ mol^{-1}.[48] We predict a noticeable difference in tautomerization for 2- and 4-thiouracil, with the former tautomerizing easier than the latter in the gas phase or in the nonpolar environment.

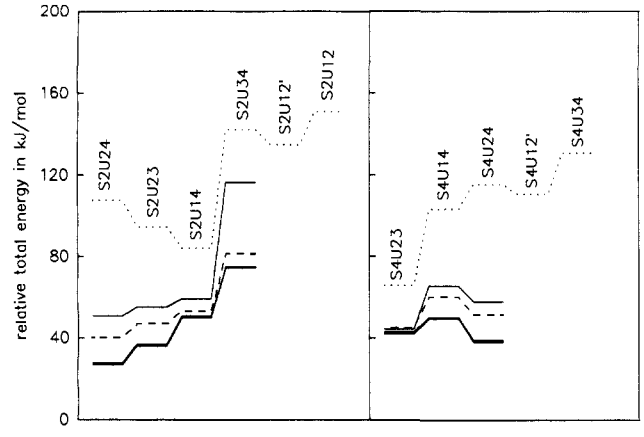
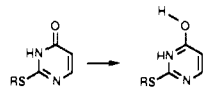
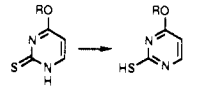
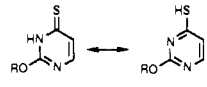
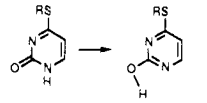
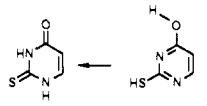
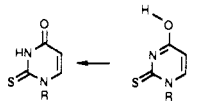
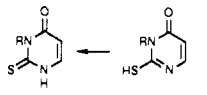


Figure 5. The relative energy of various tautomeric forms of 2-thiouracil and 4-thiouracil, in kJ mol^{-1}. The oxo–thione tautomer is taken as the reference: (···) SCF/3-21G*; (—) SCF/6-31G**; (- - -) SCF+MP2/6-31G*; (—) SCF+MP2/6-31G** plus scaled ZPE/SCF/3-21G*.

The implications of our results on the interpretation of some phenomena related to the biochemical properties can be summarized as follows. As we block the proton at the N(1) with a substituent that simulates a glycosidic linkage, we should realize that another proton at N(3) will relocate to the O(4) or S(4) atoms with a nearly equal probability, but will certainly avoid the O(2) or S(2) positions. This suggests that the formation of –S–S– cross-links between pyrimidic bases are accomplished through the S(4) rather than the S(2) atoms. With respect to the theory of point mutations, we may say that the frequency of rare 2(4)-thiouracil tautomers appearances will be as small as $\exp(-49.4/kT) \approx 2 \times 10^{-9}$, which falls into the region of estimated frequency of spontaneous point mutations (10^{-8}–10^{-11}). Thus, as in the case of uracil and 5-fluorouracil,[48] we may not exclude the

Table III. The Predicted Tautomeric Equilibria of Some Alkylated (R) Derivatives of 2-Thiouracil and 4-Thiouracil Corresponding to the Temperature $T \approx 500$ K

A	B	$E(B) - E(A)$, kJ mol^{-1}	main form	A:B
		-9.2 (1.7)[c]	4-hydroxy	1:10 (1:1)[a]
		-22.9 (-4.6)[c]	2-mercapto	A below 1% (A not detected)[b]
		-4.1 (1.7)[c]	4-mercapto	1:3
		-11.3 (-4.6)[c]	2-hydroxy	A below 1%
		27.0 (45.6)[c]	2-thione, 4-oxo	B below 1% (B not detected)[a]
		49.9 (50.2)[c]	2-thione, 4-oxo	B below 1% (B not detected)[a]
		36.2 (43.9)[c]	2-thione, 4-oxo	B below 1% (B not detected)[a]

[a] R = CH_3.[27] [b] R = neopenthoxy.[27] [c] Uracil with the DZP basis set, ref 48 and present calculations.

possibility of the formation of mismatches that involve the rare hydroxy or mercapto tautomeric forms of 2(4)-thiouracil. A nearly constant level of the mutation frequency independent from thiation or halogenation of uracil moiety is a noticeable prediction, which emerges from our calculations.

An interesting conclusion can be drawn from the present results with respect to the relative stability of several alkylated derivatives of 2(4)-thiouracil. Assuming that the substitution of a hydrogen atom for some alkyl group does not influence the stability of the respective unsubstituted (frozen) tautomers, we may predict the tautomeric equilibria of various substituted thiouraciles in the gas phase, or in the nonpolar environment at $T = 500$ K (see Table III). Our predictions are consistent with the very recent IR matrix-isolation studies[27] of 2-methylthiouracil and 4-neopentoxy-2-thiouracil. For the former, the IR spectra suggest the oxo–hydroxy equilibrium of 1:1, while our prediction is 1:10. For the latter, both theoretical and experimental data agree that 4-neopentoxy-2-thiouracil exists merely in the 2-mercapto form. The 2-thiouracil, 1-methyl-2-thiouracil, and 3-methyl-2-thiouracil exist in the oxo–thione forms according to the same study,[27] and this remains in full agreement with our theoretical estimations.

The influence of polar environment on the tautomeric equilibria can be predicted by comparing the calculated dipole moments (see Table IV). The 2(4)-thiouracil will certainly remain in the oxo–thione form in both polar and nonpolar solutions due to its substantial stability which is enhanced by the interaction with environment. Our theoretical predictions support the early UV and IR studies[5] demonstrating that 4-thiouracil, 4-thiouridine, and 5,6-dihydrouracil exist in the oxo–thione form in aqueous and nonaqueous media. However, the situation is different with some alkylated derivatives. For 2-methylthiouracil, where the dipole moments of oxo and hydroxy forms are 3.09 and 1.46 D, respectively, a polar environment will favor the oxo form. The same is true for other alkylated derivatives; thus, we may not exclude a possibility that the hydroxy forms, which dominate in the gas phase, will be replaced by the respective oxo forms in the polar environment. The problem of the tautomeric equilibria in the polar environment certainly demands a more detailed theoretical investigation and could be performed by molecular simulations based on the Molecular Dynamics or Monte Carlo methods [cf. ref 51].

Table IV. Dipole Moments (Debyes)

2-thiouracil			4-thiouracil	
tautomer		μ	tautomer	μ
S2U13	3-21G*	5.26 (4.20)[a]	S4U13	5.54 (4.47)[a]
	6-31G**	5.35		5.60
S2U24	3-21G*	1.39	S4U24	2.28
	6-31G**	1.46		1.94
S2U23	3-21G*	2.88	S4U23	4.89
	6-31G*	3.09		5.06
S2U14	3-21G*	6.47	S4U14	5.60
	6-31G**	6.65		5.59
S2U34	3-21G*	7.18	S4U34	7.67
	6-31G**	7.37		
S2U12′	3-21G*	6.75	S4U12′	
S2U12	3-21G*	8.66	S4U12	

[a] Experimental Values.[20]

Table V. IR Frequencies[a] (ν, cm^{-1}), IR Intensities (I, km mol^{-1}), Raman Activities (A, Å^4 amu^{-1}), and Raman Depolarization Ratios (d) for Stretching Modes of N1–H, N3–H, O–H, and S–H Groups of 2-Thiouracil and 4-Thiouracil[b]

	ν(N(1)–H)	ν(N(3)–H)	ν(O–H)	ν(S–H)
		2-Thiouracil		
S2U13	3462 (136/51/0.21)	3431 (112/30/0.34)		
S2U24			3533 (125/106/0.31)	2664 (1/105/0.36)
S2U23		3432 (92/47/0.34)		2671 (4/102/0.36)
S2U14	3442 (129/39/0.30)		3516 (138/109/0.37)	
S2U34		3415 (79/27/0.41)	3549 (134/114/0.32)	
S2U12′	3476 (138/65/0.26)			2671 (7/84/0.36)
S2U12	3494 (117/55/0.27)			2637 (15/106/0.36)
	3460[c]	3424[c]	3582[d]	2601[e]
		4-Thiouracil		
S4U13	3470 (183/112/0.28)	3429 (94/34/0.38)		
S4U23		3422 (118/36/0.46)	3544 (214/137/0.32)	
S4U14	3456 (127/97/0.30)			2662 (3/95/0.36)
S4U12′	3473 (250/112/0.30)		3537 (168/86/0.36)	
S4U24			3548 (141/125/0.31)	2662 (3/99/0.35)
S4U34		3449 (83/43/0.33)		2652 (3/97/0.36)

[a] Theoretical values scaled by 0.91.[46] [b] ν is the top value; $I/A/d$ values are given in parentheses. [c] 2-Thiouracil, vapor, $T = 500$ K.[27] [d] 2-Methylthiouracil, vapor, $T = 500$ K.[27] [e] 4-Neopentoxy-2-thiouracil, Ar matrix, $T = 10$–14 K.[27]

The infrared spectra belong to the most important unique properties of nucleobases, which are frequently used for identification of pyrimidic and purinic residues in nucleic acid strands. In the present work, we calculated the harmonic frequencies and intensities of nuclear vibrational bands. Although the SCF/3-21G* force field that we used suffers from severe drawbacks (e.g. not accurate enough IR/Raman intensities, overestimated frequencies due to the unsaturated basis set and lacking the electron correlation corrections[52-54]), one may use them in a qualitative analysis of the vibrational spectra. In Table V we gathered data for the most characteristic modes, i.e. for N(1)–H, N(3)–H, O–H, and S–H stretching, and compared them with the recent experimental values.[27] More details concerning the calculated geometries, rotational constants, force constants matrix, dipole and

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Table VI. IR Frequencies (ν, cm^{-1}), IR Intensities (I, km mol^{-1}), Raman Activities (A, Å^4 amu^{-1}), and Raman Depolarization (d) Ratios for the Symmetric Stretching Mode ν(S-H) for H_2S

		ν(S-H)	I	A	d
SCF	3-21G*	2642	2	159	0.21
SCF	6-31G**	2635	4	178	0.21
MP2	6-31G**	2591	4		

polarizability derivatives are available from the authors upon request.[55] The modes presented in Table V can be used in the analytical identification of various tautomeric forms by IR/Raman spectroscopy. The overall agreement with the matrix isolation data is reasonable. Following the data presented in Table V, the S-H mode intensity in the IR spectra should be almost two orders of magnitude smaller than that of the Raman intensity, which may suggest that the S-H mode can hardly be visible in IR but should be active in Raman. In order to understand the S-H vibrations and their activities, we performed benchmark SCF/3-21G*, SCF/6-31G**, and MP2/6-31G** calculations for the symmetric stretching S-H mode in H_2S (Table VI). Upon examining the results, one sees that regardless of the method the IR intensities for the symmetric vibrational mode remain small. This seems to suggest that the low IR intensity of the S-H stretching in thiouracils is not an artifact of the SCF/3-21G* approximation. This would also mean that Raman will be more suitable than IR for an identification of mercapto tautomeric forms. On the other hand (somewhat surprising in view of the present study), in the low-temperature (T = 10-14 K) matrix-isolation IR spectra for the 4-neopentoxy-2-thiouracil, a strong single peak in the 2700-2500 cm^{-1} region has been observed and interpreted as the S-H stretching.[27]

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Registry No. 2-Thiouracil, 141-90-2; 4-thiouracil, 591-28-6.

(55) Bitnet code LUDWIK@ARIZRVAX or ALES@ARIZRVAX.

Butadiene. 1. A Normal Coordinate Analysis and Infrared Intensities. Structure of the Second Rotamer

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Abstract: The question of the structure of the second stable conformer of butadiene (cis or gauche) has been reexamined by using a combination of theoretical and experimental methods. High level MP3/6-311+G**//MP2/6-31G* ab initio calculations predicted the gauche conformer to be energetically preferred by 0.98 kcal/mol (0.85 kcal/mol after correction for zero-point energies) over the cis conformer. Experimental data were reexamined as follows. An ab initio derived force field for *s-trans*-butadiene was fit to the observed gas-phase infrared and Raman spectra. Infrared intensities for *s-trans*-butadiene were measured and converted to dipole moment derivatives with respect to the internal coordinates, and the derivatives were compared to those obtained theoretically. The intensity data proved useful in determining the form of the normal coordinates for the out-of-plane bending modes. These data should prove useful in comparisons with force fields and dipole moment derivatives for other alkenes. The scaling factors obtained in the normal coordinate analysis were transferred to the calculated force fields for the cis and gauche forms, and the vibrational spectra were derived from these data. The ratios of dipole moment derivatives between experiment and theory, along with the calculated derivatives for the other rotamers, were used to predict intensities for both *cis*- and *gauche*-butadiene. The constructed spectra for the minor rotamers were compared to the experimental spectra. *gauche*-Butadiene was found to fit the data better than the cis conformer, in agreement with ab initio calculations. Vertical transition energies for the π to π^* ($A_g \rightarrow B_u$) transition for cis, gauche, and trans rotamers were calculated. While absolute transition energies were 5-10% too large, relative energies (with an origin corrected to *trans*-butadiene) supported a gauche conformer -5 to +10 nm to the red of the trans form and a cis form nearly 30 nm to the red. Although the second conformer was previously reported to be 14 nm to the red of the trans form, new experimental data suggested this gap may be only 3 nm. Significantly, both assignments of λ_{max} were in agreement with a twist angle near 25-35°. This correlation of λ_{max} to twist angle was supported empirically with the known data for cycloheptadiene and cyclooctadiene.

1. Introduction

As one of the simplest of the π-conjugated systems, butadiene has received extensive study both experimentally and theoretically. Despite these studies, some important questions remain unresolved: (1) What is the structure of the second rotamer? (2) What is the origin of the 3.5 kcal/mol stabilization of butadiene which is found in hydrogenation studies?[1] (3) What is the origin of the 4-5 kcal/mol rotational barrier?[2] We shall attempt to answer the first question herein, and we shall consider the other two related questions subsequently.

It has long been recognized that butadiene exists primarily in the *s*-trans form, and it has been believed that a second rotamer also exists. The question of the structure of the less stable isomer of butadiene is still in doubt. Is it *s*-cis or *s*-gauche? The structural question has been the subject of numerous experimental[3-6] and

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