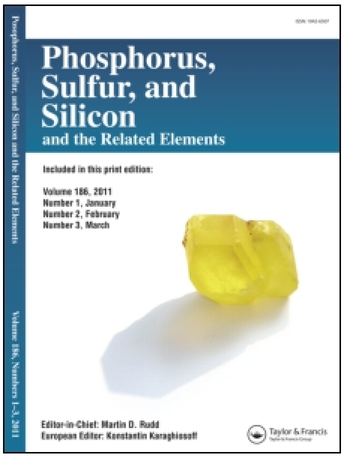

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Electronic Absorption Spectra of Some 2-Thiouracil Derivatives

H. Moustafa[a]; M. F. Shibl[a]; R. Hilal[a]
[a] Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt

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Electronic Absorption Spectra of Some 2-Thiouracil Derivatives

H. Moustafa
M. F. Shibl
R. Hilal
Chemistry Department, Faculty of Science, Cairo University,
Giza, Egypt

The electronic absorption spectra of 2-thiouracil and some of its derivatives were investigated using polar and nonpolar solvents. The present analysis is facilitated via computer deconvolution of the observed spectra and molecular orbital (MO) computations. Comparison between the experimentally observed and theoretically computed spectra in addition to a quantitative assignment of all transitions observed were undertaken. The computed dipole moments are used to indicate the polarity of the excited state and hence predict its solvent dependence. The spectra are, in general, very well predicted and assigned using INDO/S computational results. The spectrum of the trifluoro derivative is much more complicated and the corresponding states show much more solvent dependence than those observed for other thiouracil studied.

Keywords Computer decovoluation of spectra; INDO/S calculations; solvent effect; thiouracil derivatives; UV spectra

INTRODUCTION

2-Thiouracil and its derivatives are currently subjected to an extensive investigation and a wide range of activities.[1–5] For many years, thiouracils have been used as carcinogen, neoplastigen, tumorigen, and tetragen agents. Thiouracil inhibits hyperthyroidism,[6–8] virus and bacterial growth by causing alterations in protein synthesis,[9–11] kidney stone formation inhibition,[12] antithyroid activity,[13] anticancer,[14] antidote properties for mercury poisoning, and some derivatives affect the conformation of a helix through the changes in the hydrogen bonding and stacking interactions.[15]

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Address correspondence to H. Moustafa, King Abdualaziz University, Faculty of Science, Chemistry Department, 80203 Jeddah 21589, Saudi Arabia. E-mail: hmamoustafa@hotmail.com and hmamoustafa@yahoo.com

Matrix isolation I.R. spectroscopy is a very suitable technique for investigating the H-bonding ability of a large series of uracil and thiouracil derivatives.[16-17] For 2- and 4-thiouracils, Rostkowska et al. (1900)[18] have demonstrated that only the oxo-thione form is present in low temperature matrices.

Electronic absorption and fluorescence emission spectra of uracil derivatives and thiouracil were measured at room temperature in different solvent.[19] These spectral data were used to determine their lowest-exited singlet-state dipole moments using the solvatochromic method. The data shows very satisfactory agreements between the experimental and the calculated values for uracil derivatives. In case of 2-thiouracil, the calculated dipole moment is approximately 27% higher than the experimental value.

The effect of solvents of different polarities and hydrogen bonding ability on the electronic absorption and fluorescence emission spectra were investigated.[20] For 5-fluorouracil, 5-chlorouracil, 5-bromouracil, 5-iodouracil and 2-thiouracil, the absorption band maxima are generally red and shift from a low polarity solvent, such as dioxane, to a highly polar one, such as dimethyl sulphoxide. This indicates that the long-wavelength band of these pyrimidines is the result of a π–π^* transition. This assignment is also supported by the fact that the molar absorption coefficients are larger than 10^4 L mol^{-1} cm^{-1} in almost all solvents. On the other hand, the absorption spectrum of uracil is slightly blue-shifted from solvents with a low dielectric constant such as dioxane, ethyl ether, or ethyl acetate, to highly polar solvents, such as dimethyl formamide or dimethyl sulphoxide. Moreover, the molar absorption coefficients are significantly lower than the derivatives, ranging between 10^2 and 10^4 L mol^{-1} cm^{-1}, depending on the solvent. This may be due to mixing of n–π^* transition with π–π^* transition in the lowest-wavelength absorption band of these pyrimidines ($\lambda_{\max}$ 256–289 nm). Such an assignment in the case of uracil has also been postulated by Becker and Kogan (1980)[21] to explain its fluorescence properties.

The effect of 5-chloro, 5-methyl, and 2-thio substituents on the separation of electronic charges in uracil seems to be more marked in the exited singlet state than in the ground state. Indeed, although the ground-state dipole moments of uracil, its 5-halo, 5-methyl, and 2-thio substituted derivatives are quite close to each other, the exited singlet-state dipole moments of these monosubstituted derivatives are noticeably higher than that of uracil.

In our pervious work[22] of the ground-state geometries of uracil, 6-hydroxy-uracil, 6-hydroxy-, 6-amino-, 6-trifluoro-, 6-methyl-, and 6-phenyl-2-thiouracil were optimized at the Hartree-Fock level. The molecular structures were fully optimized using the 6-31G and 6-31G* basis sets. The effect of subsistent on the geometry and electronic structural features of 2-thiouracil were examined. The perturbation effects of the OH and NH_2 groups are by far more pronounced on the geometric features and the dipole moment magnitude and direction of 2-thiouracil. The potential energy per atom criteria was used to compare the relative tightness of binding in the studied series. Proton affinity and deprotonation enthalpy on each of the possible sites in 2-thiouracil and its derivatives have been calculated at the 6-31G/MP2 level of theory. The obtained results show that thiouracils behave as bases where they possess a high tendency to abstract protons. Subsistent in the 6-position have the general effect on enhancing the basic strength of thiocarbonyl site in the order $Ph < CH_3 \cong NH_2 < OH$. The CF_3 group has the effect of considerably reducing the basicity strength and enhances the acidity strength at both N1 and N3.

The above shows that while a number of studies have been undertaken to study the electronic spectra of pyrimidines, no systematic study of substituent and solvent effects on the observed spectra have been done. Such a study is critically important to understand their electronic structure and might very well lead to understanding the origin of their biological activity.

In the present work, a comparative investigation of the electronic absorption spectra of a series of 2-thiouracils is presented. The present analysis involves both computer deconvolutions of the observed spectra and MO computations.

EXPERIMENTAL

Solvents and Compounds

Solvents used throughout this work are absolute ethanol (Aldrich) and 1,2-dichloroethane (Aldrich, USA).

Compounds studied in the present work are all analytical grade reagents (Merck, USA and/or BDH) and used without further purification. The studied compounds are uracil, 6-hydroxy uracil, 2-thiouracil, 6-hydroxy-2-thiouracil, 6-amino-2-thiouracil, 6-methyl-2-thiouracil, 6-trifluoromethyl-2-thiouracil and 6-phenyl-2-thiouracil.

Apparatus

All spectra were taken using a Perkin Elmer (USA) Lambda 4B UV/VIS spectrophotometer through the wavelength range 190–900 nm using 1.0 cm-fused silica cells.

Computers and Computer Programs

All computations were done on digital dec station 5000/50 under Ultrix. The optimized geometries obtained using the 6-31G and 6-31G* basis sets were used to compute the electronic absorption parameters. Computed electronic spectra were done using the program INDO/S developed and tested in our laboratory.[23] Computer deconvolutions of the observed spectra are calculated using MathCAD7 (professional edition) under windows 98.[24]

RESULTS AND DISCUSSION

The Electronic Spectra of 2-Thiouracil

Figure 1 presents the electronic absorption spectra of 2-thiouracil in dichloroethane (A) and ethanol (B) and shows definite dependence on the solvent polarity. Two absorption regions are recognized: a broad medium intensity envelope that covers the 300–250 nm region and a short wavelength absorption in the 200–220 nm region. Computer deconvolution of the spectrum (Figure 1) shows that the long wavelength envelope encloses two main absorption transitions centered at 267 and 300 nm, respectively, in the polar solvent. Decreasing solvent polarity shifts these two bands in opposite directions. Thus, the long wavelength absorption undergoes a marked blue shift of about 12 nm, whereas the second band experiences a slight red shift of about 4 nm with the net result of merging both bands to an extent greater than that in the case of polar solvent. Furthermore, solvent polarity has a pronounced effect on the relative intensities of these two absorption bands. Thus, while increasing solvent polarity decreases the intensity of all bands, the relative ratios of the two bands are reversed.

Table I presents a comparison of the experimentally-observed and theoretically-computed spectra in addition to a quantitative assignment of all transitions observed. The long wavelength absorption is due to a transition to a state with a slightly smaller dipole moment and is composed of a mixture of the $\phi_{20}^{-1}\phi_{22}$ and the $\phi_{20}^{-1}\phi_{23}$ configurations, with the former configuration as the main contributor. The MO ϕ_{20} is localized to a large extent on the sulphur atom, whereas, the MO's ϕ_{22} and ϕ_{23} are both delocalized to a considerable extent on the heterocyclic ring. Thus, the $S_o \rightarrow S_1$ transition involves a considerable CT character opposite to the dipole moment vector. Therefore, polar solvents will stabilize the ground state to a much greater extent and this explains the observed blue shift upon increasing solvent polarity.

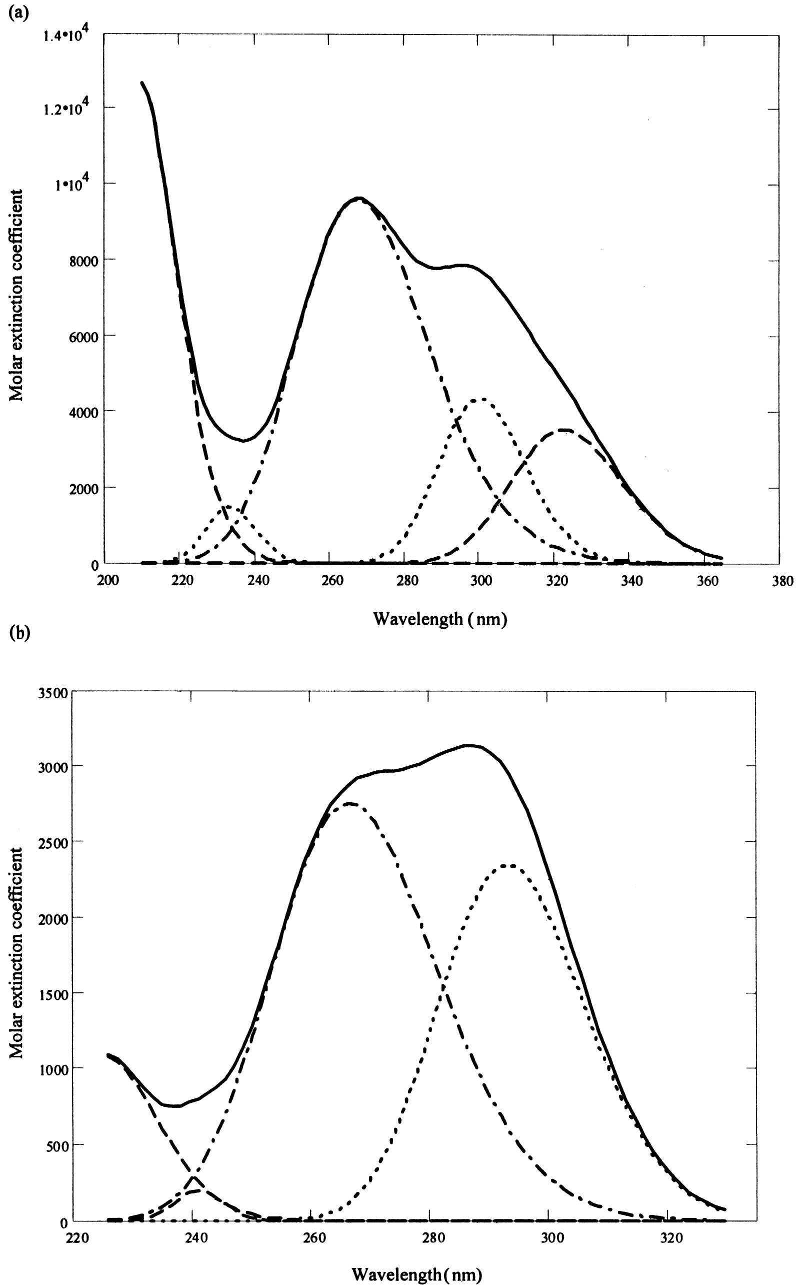

FIGURE 1 Electronic absorption spectra of 2-thiouracil and its Gaussian analysis measured in (a) 1,2-dichloroethane and (b) ethanol.

TABLE I Theoretically Computed and Experimentally Observed Transition Energies and Intensities for 2-Thiouracil

Theoretical						Experimental			
						1,2-Dichloroethane		Ethanol	
State	Configuration	Coefficient	λ, nm	μ	f	λ, nm	f	λ, nm	f
I	20–22	0.6058	292.5	6.02	0.460	293.3	0.036	322.6	0.055
	20–23	0.3424							
II	20–22	0.3354	265.0	11.62	0.052	266.7	0.053	300.3	0.060
	20–23	0.6174				241.0	0.002	267.5	0.255
III	19–22	0.6246	231.3	11.15	0.016	224.7	0.021	233.4	0.020
IV	19–23	0.6205	212.5	6.91	0.709			209.2	0.217

The second $(\pi, \pi^*)^1$ state is a mixture of the same two configurations, yet the weight of the $\phi_{20}^{-1}\phi_{23}$ configuration is much higher. This CT state is much more polarized than the ground state ($\mu \cong 11.62$ D) and hence is expected to be stabilized in polar solvents to an extent greater than that of the ground state. This would lead to a red shift in agreement with the observed trend.

The shortest wavelength $(\pi, \pi^*)^1$ state is predicted at ~ 212 nm with a very strong intensity ($f = 0.71$) in very good agreement with experiment. This state is composed of a major configuration of $\phi_{19}^{-1}\phi_{23}$ which is a charge-transfer transition onto the heterocyclic ring. This $(\pi, \pi^*)^1$ state almost possesses the same polarity as the ground state, and hence no pronounced solvent effect on band position is expected.

The electronic absorption spectrum of 2-thiouracil is quite different from that of its oxygen analogue, uracil. The latter shows only one main absorption band at $\sim$258 nm which is almost unaffected by solvent polarity. Thus, replacement of oxygen by sulphur alters the electronic energy states considerably. Careful inspection of the two low-laying singlet $(\pi, \pi^*)^1$ state of 2-thiouracil shows that both are composed of the same two configurations, viz., $\phi_{20}^{-1}\phi_{22}$ and $\phi_{20}^{-1}\phi_{23}$. The highest occupied molecular orbital (HOMO), ϕ_{20}, is a localized MO on the thiocarbonyl moiety with its major charge density around the more electronegative sulphur atom. The HOMO in the case of uracil is, however, a delocalized MO over the carbonyl and the heterocyclic ring. This delocalization stabilizes the MO to an extent greater than in case of the localized HOMO of 2-thiouracil. As a consequence of this strong interaction, the LUMO of uracil is lifted over destabilization than that of 2-thiouracil. The net result of the orbital interaction, in case of uracil, is the increase in the HOMO–LUMO energy gap and blue shift of the obsereved electronic transition.

Substitutent Effects

In the following the effect of substituent of different electron-donating(withdrawing) powers will be investigated.

The Electronic Spectra of 6-Methyl 2-Thiouracil

Figure 2 presents the electronic absorption spectra of 6-methyl-2-thiouracil in ethanol and 1,2-dichloroethane as solvents. Computer deconvolution of the spectrum shows the presence of two main absorption bands enclosed under the main envelope and centered at 285 and 259 nm. The effect of methyl substitution on the observed spectrum is intensification and slight perturbation of band position; this is typical behavior due to its inductive effect. The long wavelength absorption is composed of one main configuration the $\phi_{24}^{-1}\phi_{25}$ which is a delocalized transition involving a slight migration of charge opposite to the dipole moment vector. Hence, this $(\pi, \pi^*)^1$ state would experience blue shift upon increasing solvent polarity, which is in agreement with the experiment.

The second $(\pi, \pi^*)^1$ state is also composed of one main transition $\phi_{24}^{-1}\phi_{26}$ configuration. This configuration involves charge transfer in the same direction as the dipole moment vector and hence a red shift is expected upon increasing solvent polarity. Thus, the extent of overlap and merging of the two long wavelength bands in the spectrum of 6-methyl-2-thiouracil is predicted to increase upon increasing solvent polarity. This is in agreement with experimental observations.

The short wavelength absorption centered at 213 nm (in ethanol) is composed of one major configuration, $(\phi_{22}^{-1}\phi_{26})$, which is a CT transition involving migration of charge opposite to the dipole moment vector.

It is interesting to notice that methyl substitution in the 6-position has almost no effect on the energies of the frontier orbital as compared to the parent thiouracil (cf. Figure 1). Its perturbation effect manifests itself in the slight intensification of the observed transitions and loss of resolution of the long wavelength broad envelope.

The three compounds studied so far, namely uracil, 2-thiouracil, and 6-methyl-2-thiouracil, are all π-isoelectronic. Now, if an —OH group is substituted into the 6-position of 2-thiouracil, an extension of the π-system takes place, which is expected to manifest itself on the observed spectrum.

The Electronic Spectra of 6-Hydroxy-2-thiouracil

Figure 3 presents the electronic absorption spectra of 6-hydroxy-2-thiouracil in polar and nonpolar solvents. The general feature of the spectrum appears different from the parent compound. The spectrum

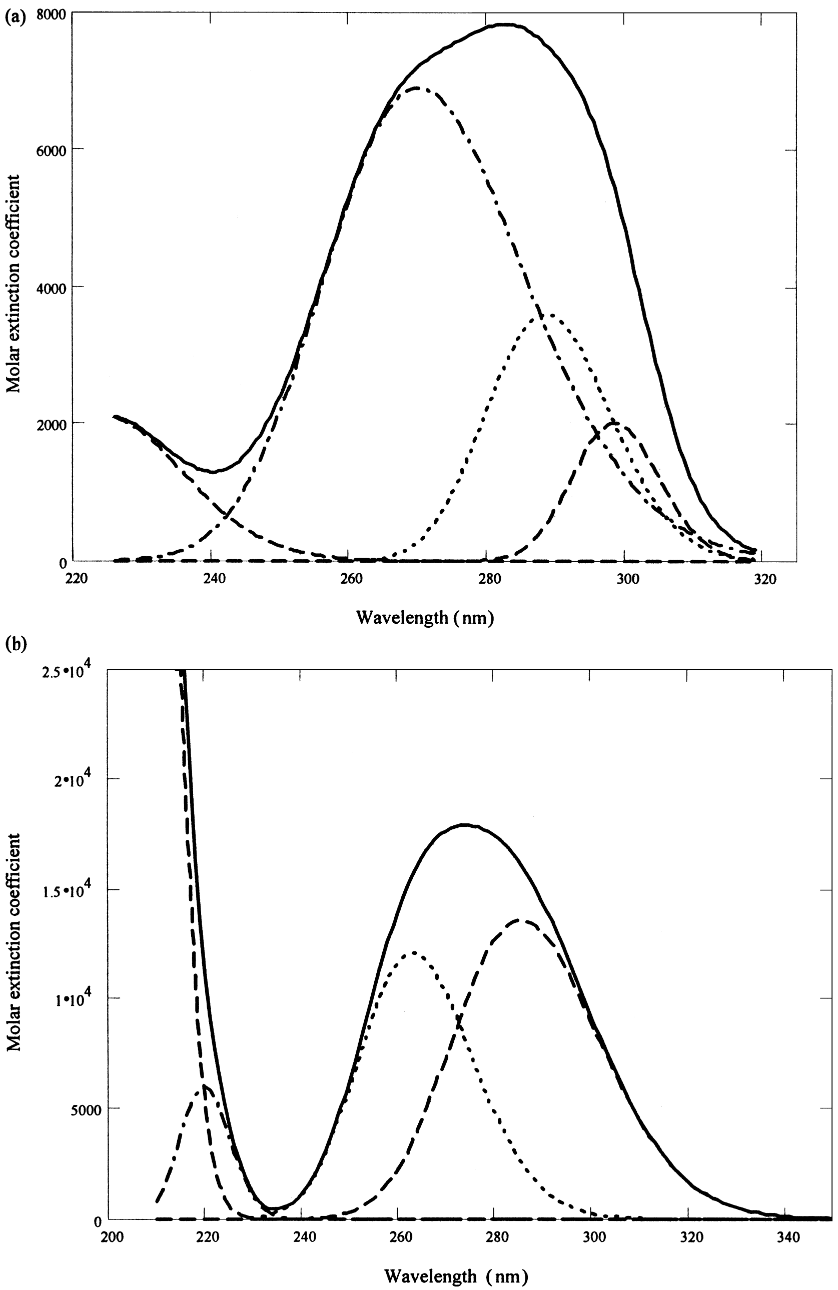

FIGURE 2 Electronic absorption spectra of 6-methyl-2-thiouracil and its Gaussian analysis measured in (a) 1,2-dichloroethane and (b) ethanol.

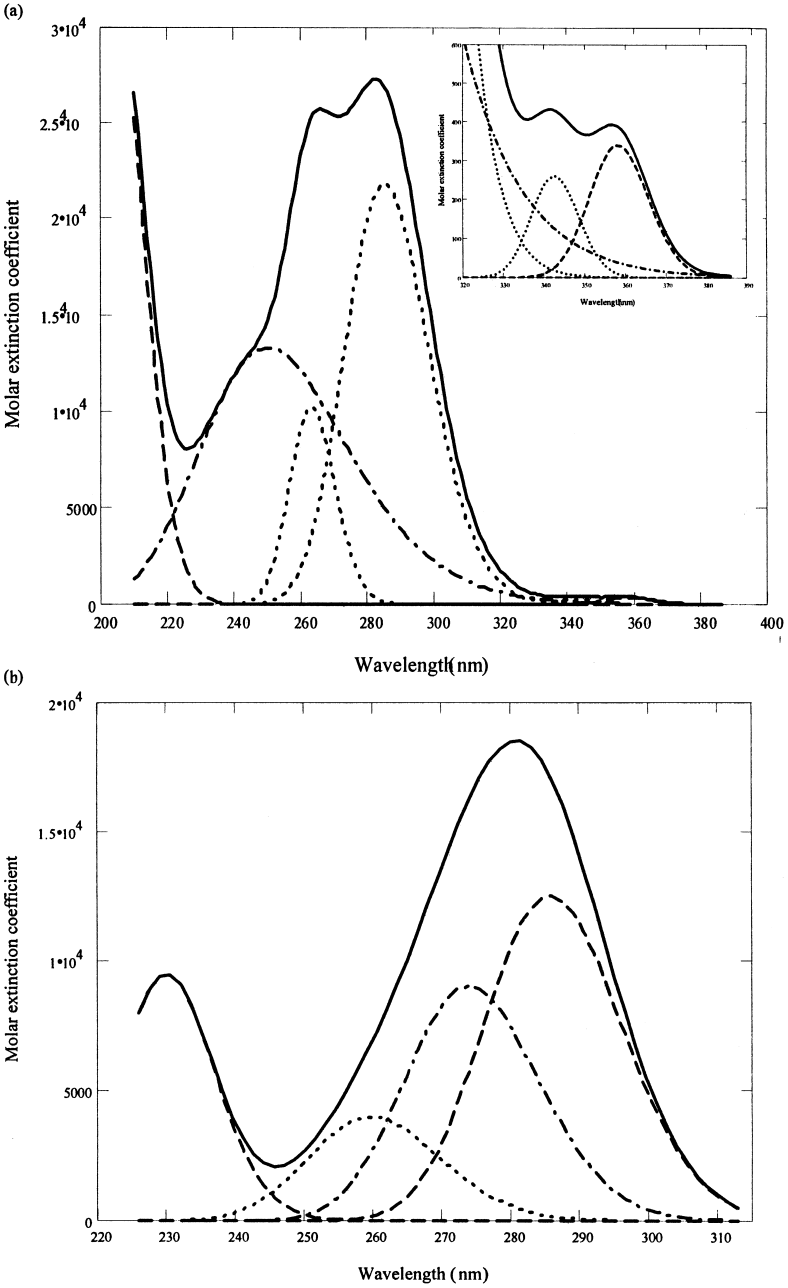

FIGURE 3 Electronic absorption spectra of 6-hydroxy-2-thiouracil and its Gaussian analysis measured in (a) 1,2-dichloroethane and (b) ethanol.

shows two main absorption regions are observed; a long wavelength absorption that covers the 320–360 nm range and a much more intense absorption below 300 nm. Computer deconvolution of the spectrum shows the presence of two overlapping low-intensity absorption bands under the long wavelength envelope. The vibrational structure and the low intensity ($\varepsilon \sim 200$) of these bands suggest their n $\rightarrow \pi^*$ origin. These bands are not observed in nonpolar solvents, most probably because of their reduced intensity and the low solubility in nonpolar media. The 230–300 nm envelope deconvoluted into three main absorption bands, which are well resolved and of strong intensity. In addition, a short wavelength and a very strong band is deconvoluted at ~205 nm. These four bands may be safely assigned as π–π^* transitions.

Table II compares the experimentally-observed and theoretically-computed transition energies and intensities. The four $(\pi, \pi^*)^1$ states are well reproduced theoretically. The first $(\pi, \pi^*)^1$ possesses a dipole moment slightly greater than that of the ground state. This polar state is composed of one main configuration, $\phi_{24}^{-1}\phi_{25}$, which is a delocalized transition and is not expected to show any appreciable solvent dependence.

The second $(\pi, \pi^*)^1$ state is by far much more polar than the ground state and also is composed of one main configuration, $\phi_{24}^{-1}\phi_{26}$. This CT transition is in the direction of the dipole moment vector and hence the corresponding absorption band enjoys a marked red shift upon increasing solvent polarity.

The third $(\pi, \pi^*)^1$ state is also a polar, one-configuration ($\phi_{22}^{-1}\phi_{25}$) state which also shows high solvent dependence. Finally, the short wavelength and very strong absorption is predicted to be slightly less polar than the ground state and is expected to show no marked solvent dependence.

TABLE II Theoretically Computed and Experimentally Observed Transition Energies and Intensities for 6-Hydroxy-2-thiouracil

						Experimental			
Theoretical						1,2-Dichloroethane		Ethanol	
State	Configuration	Coefficient	λ, nm	μ	f	λ, nm	f	λ, nm	f
I	23–25	0.6652	437.7	8.52	0.000	285.7	0.163	358.2	0.000
II	24–25	0.6796	292.8	6.86	0.436	274.0	0.099	342.5	0.001
III	24–26	0.6785	259.7	12.34	0.119	259.7	0.052	285.3	0.367
IV	22–25	0.6819	239.5	10.22	0.027	229.9	0.131	263.2	0.081
V	22–26	0.6734	219.4	6.16	0.647			250.0	0.512
								205.4	0.416

Contrary to the case of the four $(\pi, \pi^*)^1$ states, the $(n, \pi^*)^1$ states are theoretically poorly reproduced. The difference being ~ 0.8 eV is much greater than expected. Both bands are due to the $\phi_{23}^{-1}\phi_{25}$ transition. The MO ϕ_{23} is a nonbonding MO localized on the sulphur atom, whereas, the π-MO ϕ_{25} is delocalized over the entire molecule. This symmetry-forbidden, vibronically-allowed transition is theoretically predicted at a much longer wavelength due to the overestimation of the nonbonded interaction between the sulphur lone-pair orbital and the low lying nonbonding MO involving the oxygen atoms. This exaggerated interaction lowers the later MO and elevates the lone-pair orbital of sulphur, thus decreasing n–π^* transition energy. This seems to be an inherent disadvantage of intermediate neglect of differential overlap (INDO), as in any model based on neglecting the differential overlap especially, the three- and four-center terms. It is worth noting that the spacing of the vibrational fine structure of the $(n, \pi^*)^1$ transition is 1064 cm^{-1} which corresponds to the ring out of phase vibration.

The Electronic Spectra of 6-Hydroxy Uracil

The spectrum of 6-hydroxy uracil (barbeturic acid) is presented in Figure 4. The similarity between this spectrum and that of its π-isoelectronic analogue 6-hydroxy-2-thiouracil is striking. Thus, whereas the spectrum of uracil is of much reduced intensity, diffused and blue-shifted as compared to that of 2-thiouracil, 6-hydroxy substitution introduces appreciable electronic effects into the heterocyclic ring and alters the ordering of the MO's considerably.

The Electronic Spectra of 6-Amino-2-thiouracil

The spectrum of the π-isoelectronic molecule 6-amino-2-thiouracil is presented in Figure 5 in the polar solvent. Low solubility in nonpolar solvents prevent the recording of its spectrum in such solvents. The main features of this spectrum are the same as that of the 6-hydroxy derivative. Indeed, the four $(\pi, \pi^*)^1$ states observed correspond very well to those observed in the spectrum of 6-hydroxy derivative. The third and fourth $(\pi, \pi^*)^1$ states involve slightly more CT character and are red-shifted as compared to those observed in the spectrum of the hydroxy derivative. The correspondence between the theoretically-computed and the experimentally-observed transition energies is satisfactory. However, the INDO/s method failed again to predict the transition energies of the $(n, \pi^*)^1$ states. The spacing of the vibrational fine structure of the $(n, \pi^*)^1$ manifold is $\sim$1040 cm^{-1} which corresponds very well to the value predicted for the 6-hydroxy derivative and elaborates upon our previous assignment to the out-of-phase ring vibration.

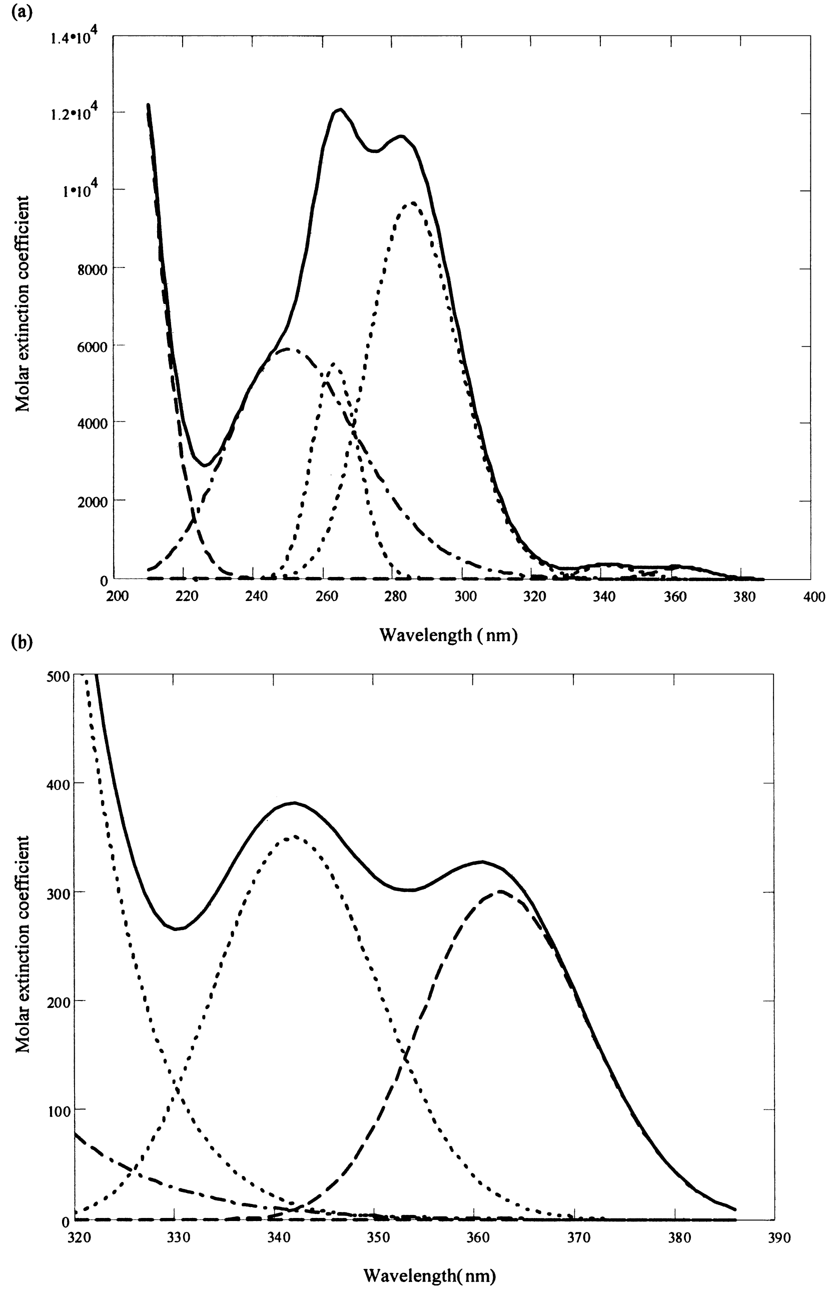

FIGURE 4 Electronic absorption spectra of 6-hydroxy-uracil and its Gaussian analysis measured in (a) 1,2-dichloroethane and (b) ethanol.

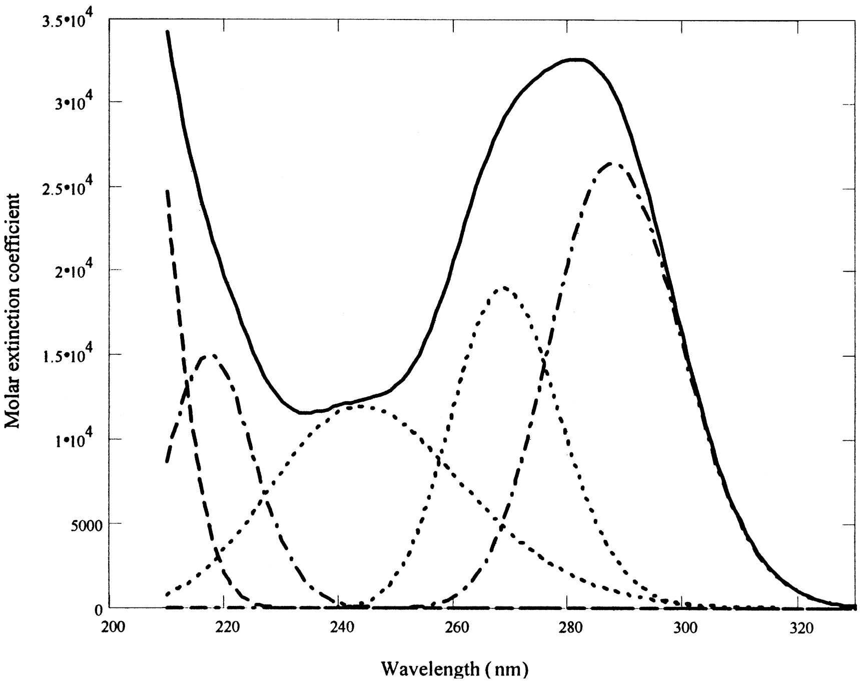

FIGURE 5 Electronic absorption spectra of 6-amino-2-thiouracil and its Gaussian analysis measured in ethanol.

All subsistents studied so far are electron-donor subsistent, which interact with the heterocyclic ring either by inductive and (or) extended conjugation via p_{π} lone-pair orbital. It is interesting to investigate the effect of a strong electron-withdrawing substituent such as the $-CF_3$ group. The uracil heterocyclic ring is an electron-rich environment and the π-electron system is highly polarized in a direction opposite to the polarization of the σ-frame work.

The Electronic Spectra of 6-Trifluoromethyl-2-thiouracil

The spectrum of 6-trifluoromethyl-2-thiouracil is presented in Figure 6 in polar as well as in nonpolar solvents. The spectrum is composed of three main manifolds and the long wavelength envelope is broad and diffuse. Computer deconvolution of the spectrum shows the existence of four main band systems. The longest wavelength band at 345 nm is very weak ($\varepsilon \sim 600$) and is broad and diffuse. This band may be assigned as an $(n, \pi^*)^1$ transition. Its diffuse nature made it impossible to estimate the frequency of the associated vibrational mode. Theoretically, an n, π^* state is predicted at 442 nm, in very bad agreement

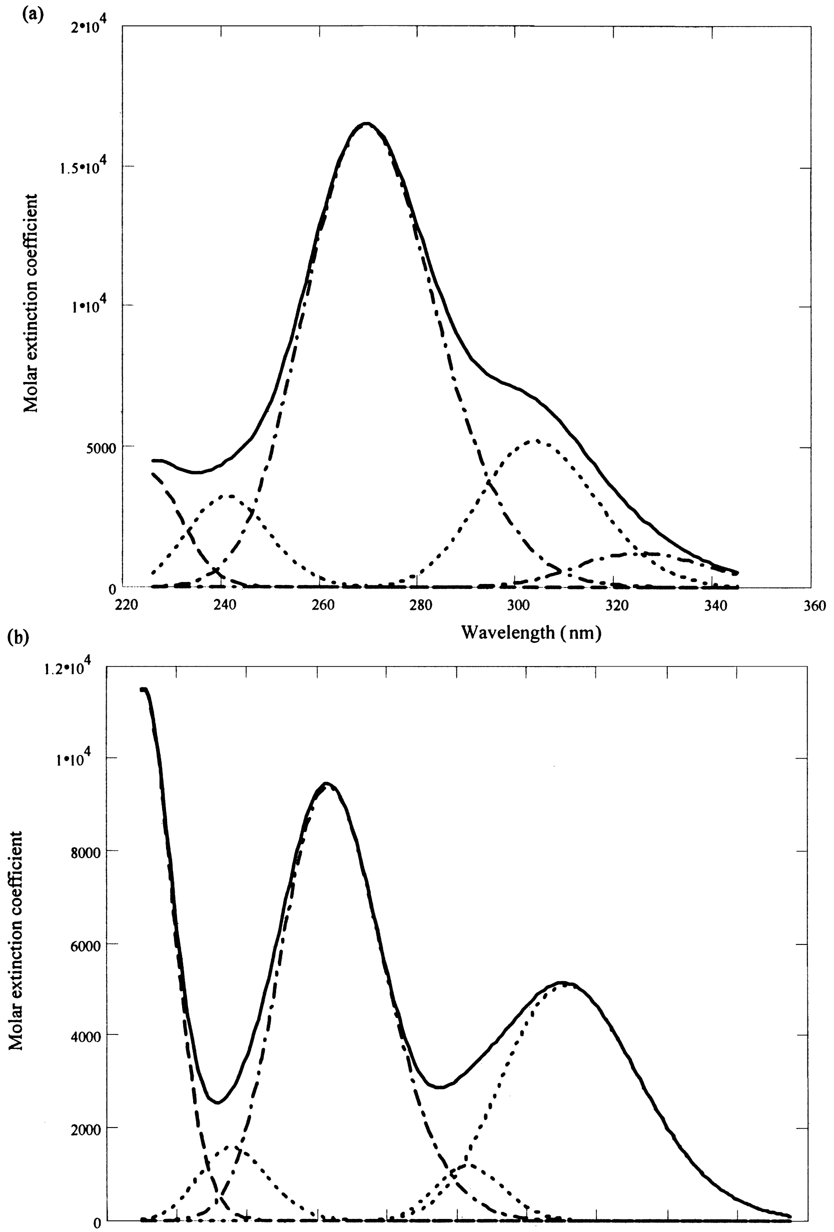

FIGURE 6 Electronic absorption spectra of 6-trifluoromethyl-2-thiouracil and its Gaussian analysis measured in (a) 1,2-dichloroethane and (b) ethanol.

with experiment. This seems to be a general disadvantage of the INDO/s Hamiltonian. The (n, $\pi^*)^1$ state involves two main configurations, the $\phi_{33}^{-1}\phi_{34}$ and the $\phi_{33}^{-1}\phi_{35}$ configurations. ϕ_{33} is a nonbonding MO localized on the sulphur atom whereas, ϕ_{34} and ϕ_{35} MO's are π^* orbital delocalized on the heterocyclic ring. This band undergoes a considerable blue shift ongoing from nonpolar to polar solvents. Computer deconvolution of the spectrum in ethanol predicted a weak absorption band at ~305 nm hidden under the strong broad band $(\pi, \pi^*)^1$ band.

The first $(\pi, \pi^*)^1$ state is centered at ~ 300 nm in 1,2-dichloroethane as solvent. This band is predicted theoretically at 292 nm, in very good agreement with the experiment, and is a mixture of two main configurations, $\phi_{32}^{-1}\phi_{34}$ and $\phi_{32}^{-1}\phi_{35}$. Both involve CT transitions in the direction of the dipole moment vector. Therefore, this $(\pi, \pi^*)^1$ is expected to undergo red shift upon increasingly solvent polarity. The first $(\pi, \pi^*)^1$ band is red-shifted to 330 nm in ethanol as a solvent. This considerable red shift together with the corresponding blue shift of the (n, $\pi^*)^1$ state is the reason why this later state is not observed experimentally.

The second $(\pi, \pi^*)^1$ is observed at 269 nm and is predicted theoretically at exactly the same wavelength. This state is composed of the same two configurations as the first $(\pi, \pi^*)^1$ state but with inverted weights. The dipole moment of this state is slightly lower than that of the ground state and thus is predicted to show none or a slightly blue shift upon an increasingly solvent polarity which is indeed the case.

The third $(\pi, \pi^*)^1$ is observed at 230 nm as a weakly broad absorption in the short wavelength tail of the 269 nm band. This state is predicted at about the same wavelength with very low intensity ($f \cong 0.004$), and is due to the $\phi_{31}^{-1}\phi_{34}$ and the $\phi_{31}^{-1}\phi_{35}$ transitions. The polarization of this state is slightly greater than that of the ground state and thus is predicted to show a slight red shift upon increasingly solvent polarity.

A very strong, short wavelength absorption is observed at 212 nm and is predicted to be a delocalized transition that involves the same two configurations as the third $(\pi, \pi^*)^1$ but with inverted weights.

The spectrum as a whole is very well predicted and assigned using the INDO/s computational results. The spectrum of the 6-trifluoro derivative is much more complicated and the corresponding states show much more solvent dependence than those observed for other thiouracils studied in this work.

The Electronic Spectra of 6-Phenyl-2-thiouracil

To complete our investigation of substituent effect on the electronic structure and spectra of thiouracil, we extended the π-conjugated system by introducing a phenyl moiety in the 6-position. Figure 7 presents the spectrum of 6-phenyl-2-thiouracil in polar and in nonpolar

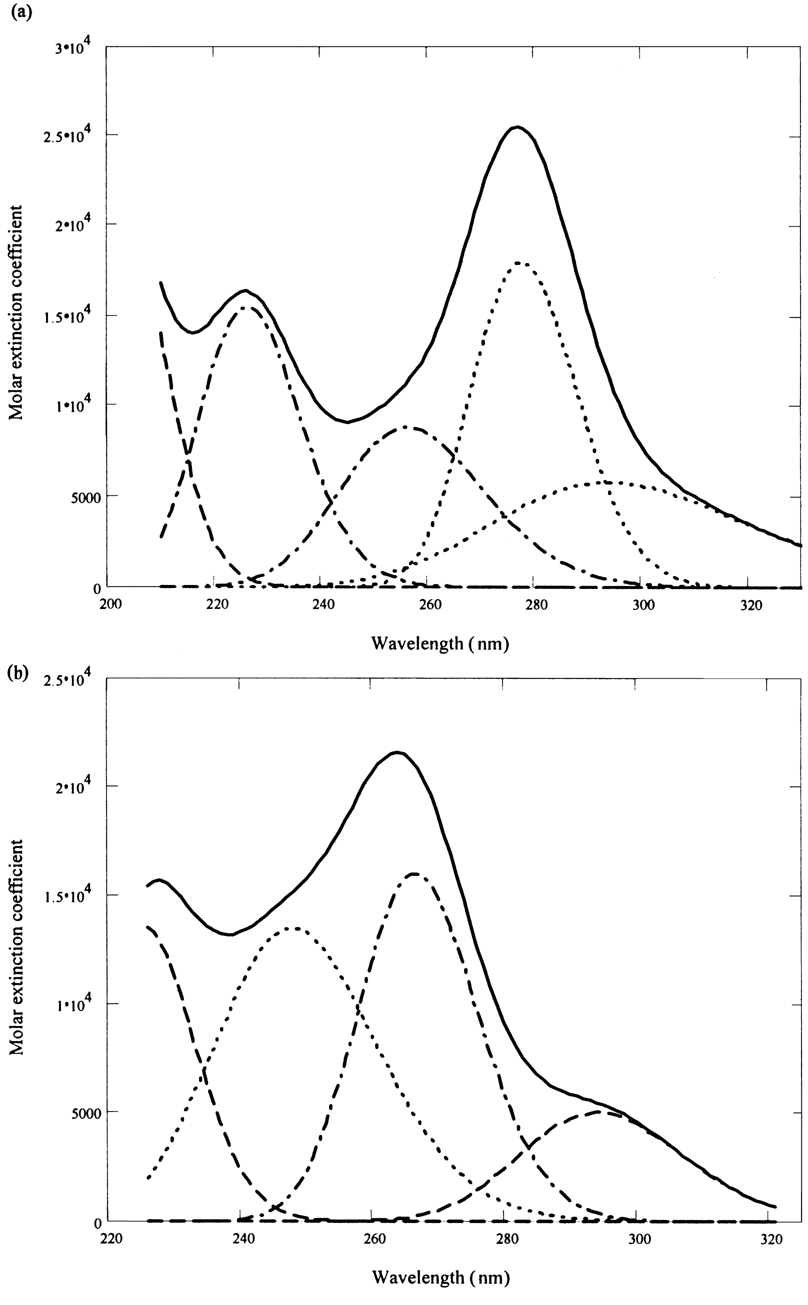

FIGURE 7 Electronic absorption spectra of 6-phenyl-2-thiouracil and its Gaussian analysis measured in (a) 1,2-dichloroethane, (b) ethanol.

solvents. The spectrum is composite and does not correspond to any one of its subsystems, which indicates a considerable conjugative interaction between them. Computer deconvolution of the spectrum shows the existence of four main band systems which all correspond to $(\pi, \pi^*)^1$ states. No $(n, \pi^*)^1$ transitions are observed in the spectrum at hand. This is expected because the n–π^* transition is symmetry forbidden and will not be observed unless some out-of-plane vibrational mode lifts this symmetry constraint. For the phenyl derivative, the tight extended π-conjugation seems to restore coplanarity and thus hinders the out-of-plane bending, which is responsible for the appearance of the n, π^* transitions in the case of other derivative.

The first $(\pi, \pi^*)^1$ state is observed at ~305 nm which is red-shifted by more than 15 nm as compared to the corresponding states of the 2-thiouracil derivatives studied earlier. This is a conjugation band which is theoretically predicted to be composed of one main configuration, the $\phi_{35}^{-1}\phi_{37}$. Both MO's are delocalized with the MO ϕ_{37} extending over the entire molecule and ϕ_{35} extending over the heterocyclic moiety. The second $(\pi, \pi^*)^1$ state is also a conjugation transition that is observed at ~275 nm and predicted theoretically to be composed of the $\phi_{35}^{-1}\phi_{36}$ configuration. Both states I and II are slightly less polarized than the ground state due to a slight shift of charge in a direction against the dipole moment vector.

The remaining $(\pi, \pi^*)^1$ states are described in Table III. It is worth noting that the fourth $(\pi, \pi^*)^1$ state is observed at 235 nm and is predicted at almost the same wavelength with a very large dipole moment. This highly polarized state is composed of one main configuration which involves the MO ϕ_{33}. Thus, it is a CT state with considerable charge transfer in the direction of the dipole moment vector.

Table III summarizes the spectral characteristics of the studied thiouracils.

TABLE IIIa Theoretically Computed and Experimentally Observed Transition Energies and Intensities for Uracil

		Theoretical			
State	Configuration	coefficient	λ, nm	μ	f
I	19–23	0.5995	298.8	6.18	0.000
II	21–22	0.6896	232.1	7.75	0.599
III	21–23	0.7023	212.7	11.07	0.232

TABLE IIIb Theoretically Computed and Experimentally Observed Transition and Energies and Intensities for 6-Methyl-2-thiouracil

Theoretical						Experimental			
						1,2-Dichloroethane		Ethanol	
State	Configuration	Coefficient	λ, nm	μ	f	λ, nm	f	λ, nm	f
I	24–25	0.6672	292.5	6.68	0.445	298.5	0.015	285.7	0.271
II	24–26	0.6713	259.9	10.95	0.093	288.6	0.042	263.2	0.192
III	22–25	0.6721	236.2	11.95	0.023	270.3	0.138	219.8	0.074
IV	22–26	0.6649	216.3	6.89	0.654	224.7	0.049	203.3	2.388

TABLE IIIc Theoretically Computed and Experimentally Observed Transition Energies and Intensities for 6-Amino-2-thiouracil

Theoretical						Experimental Ethanol	
State	Configuration	coefficient	λ, nm	μ	f	λ, nm	f
I	23–25	0.6937	431.6	8.17	0.000	287.9	0.392
II	24–25	0.6974	293.9	8.39	0.391	268.8	0.202
III	24–26	0.6543	256.6	9.02	0.307	243.9	0.372
IV	22–25	0.6862	249.7	13.09	0.071	217.4	0.250
V	22–26	0.6588	224.2	7.43	0.423	204.9	0.404

TABLE IIId Theoretically Computed and Experimentally Observed Transition Energies and Intensities for 6-Trifluoromethyl-2-Thiouracil

Theoretical						Experimental			
						1,2-Dichloroethane		Ethanol	
State	Configuration	Coefficient	λ, nm	μ	f	λ, nm	f	λ, nm	F
I	33–34 33–35	0.4728 0.5154	442.6	6.18	0.000	325.2	0.017	331.1	0.098
II	32–34 32–35	0.5650 0.4055	292.9	11.38	0.462	304.0	0.074	303.0	0.015
III	32–34 32–35	0.4028 0.5775	269.5	4.88	0.054	269.5	0.294	263.2	0.206
IV	31–34 31–35	0.5920 0.3715	233.0	10.03	0.005	241.0	0.048	235.3	0.031
V	31–34 31–35	0.3533 0.5922	215.4	5.55	0.725	225.2	0.056	210.5	0.117

TABLE IIIe Theoretically Computed and Experimentally Observed Transition Energies and Intensities for 6-Phenyl-2-thiouracil

Theoretical						Experimental			
						1,2-Dichloroethane		Ethanol	
State	Configuration	Coefficient	λ, nm	μ	f	λ, nm	f	λ, nm	F
I	34–37	0.6777	417.2	7.90	0.000	266.7	0.163	294.1	0.176
II	35–37	0.6745	289.2	7.55	0.429	249.1	0.077	277.8	0.231
III	35–36	0.6362	279.5	4.99	0.433	247.8	0.326	256.4	0.199
IV	33–36	0.6402	251.2	5.77	0.285	225.7	0.210	226.3	0.312
V	33–37	0.7040	233.4	19.83	0.116			204.1	0.276
VI	35–38	0.4561	219.9	5.83	0.240				
	33–38	0.5389							

SUMMARY AND CONCLUSIONS

The electronic absorption spectra of 2-thiouracil and some of its derivatives are investigated using ethanol as a polar solvent and dichloroethane as a nonpolar solvent. For 2-thiouracil, two absorption regions are recognized at a broad envelope in the 300–450 nm regions and a short wavelength one at 200–220 nm. Decreasing solvent polarity shifts these two bands in opposite directions, while increasing solvent polarity decreases the intensity of all bands and reverses the relative ratios of their intensities. Computer deconvoluation of the spectrum shows that the long wavelengths enclose two main absorption transitions centered at 267 and 300 nm, respectively. The spectrum of uracil shows only one main absorption band at 258 nm which is almost unaffected by solvent polarity. The effect of methyl substitution on the observed spectrum is intensified and slightly perturbed of band position, which is a typical behavior due to its inductive effect. It is interesting to notice that methyl substitution in the 6-position has almost no effect on the energy of the frontier orbital as compared to the parent thiouracil. If an OH-group is substituted into the 6-position of 2-thiouracil, the general feature of the spectrum appears different from that of the parent compound, which is a long wavelength band that cover the 300–320 nm range and a much intense one at 300 nm. The spectrum of 6-hydroxy-uracil is of much reduced intensity, diffused and blue shifted, as compared to that of 2-thiouracil, yet 6-hydroxy substitution introduces appreciable effects into the heterocyclic ring and considerably alters the ordering of the MO's. The main features of 6-amino substitution are the same as that of the 6-hydroxy derivative. The spectrum of the 6-trifluoro methyl as a strong electron withdrawing is much more complicated and the corresponding states show much more solvent dependence than those observed for electron-donating substituents. The spectrum of the composite 6-phenyl-2-thiouracil is does not correspond to any one of its substituents, which indicates a considerable conjugative interaction between them.

REFERENCES

[1] J. Elguero, C. Marzin, A. R. Katritzky, and P. Linda, The Tautomerism of Heterocycles, A. R. Katritzky and A. J. Boulton, eds. (Academic Press, New York, 1976), Suppl. 1.

[2] A. L. Lehninger, Short Course in Biochemistry (Wiley, New York 1973) p. 21.

[3] A. R. Katritzky, *Chimia*, **24,** 134 (1970).

[4] N. W. Strickberger, Genetics, in *Advances in Heterocyclic*, J. M. Lagowski, ed. (MacMillan Publishers Ltd., England, 1969), p. 338.

[5] A. R. Katritzky and J. M. Lagowski, in *Advances in Heterocyclic Chemistry*, A. R. Katritzky and A. J. Boulton, eds. (Academic Press, New York, 1963), Vol. 1, p. 400.

[6] E. B. Astwood, A. Bessel, and A. M. Hughes, *Endocrinology*, **37,** 456 (1945).

[7] W. H. Miller, R. O. Roblin, and E. B. Astwood, *J. Am. Chem. Soc.*, **67,** 2201 (1945).

[8] R. H. Williams and G. W. Bissel, *Science*, **98,** 156 (1943).

[9] R. Heemer and J. Rosseels, *Biochim. Biophys. Acta*, **11,** 438 (1953).

[10] R. Hammers, *Biochim. Biophys. Acta*, **21,** 170 (1956).

[11] C. F. Beck and G. J. Howlett, *J. Mol. Biol.*, **111,** 1 (1977).

[12] W. O. Foye, Y. L. Lai-Chen, and B. R. Patel, *J. Pharm. Sci.*, **70,** 49 (1981).

[13] E. Gaitan, R. C. Cooksey, D. Matthews, and R. Presson, *Trace. Subt. Environ. Health*, **15,** 247 (1981).

[14] M. Altweg and E. Kubli, *Nucl. Acid Res.*, **8,** 215 (1980).

[15] A. Les and L. Adamowicz, *J. Am. Chem. Soc.*, **112,** 1504 (1990).

[16] G. Maes and Th. Zeegers-Huyskens, *J. Mol. Struct.*, **100,** 305 (1983).

[17] J. P. Perchard, A. J. Barnes, W. J. Orville-Thomas, A. Muller, and R. Gaufres (Eds.), *Matrix Isolation Spectroscopy* (Reidel, Dordrecht, 1981).

[18] H. Rostkowska, K. Szczepaniak, M. J. Nowak, J. Leszczyski, K. Kubulat, and W. B. Person, *J. Am. Chem. Soc.*, **112,** 2147 (1900).

[19] C. Parkanyl, C. Bonfiaa, J. J. Aaron, M. D. Gaye, L. Szentpaly, R. Ghosh, and K. S. Raghuveer, *J. Structural Chem.*, **3,** 277 (1992).

[20] W. C. Schneider and I. F. Halverstadt, *J. Am. Chem. Soc.*, **70,** 2626 (1948).

[21] R. S. Becher and G. Kogan, *Photochem. Photobiol.*, **31,** 5 (1980).

[22] H. Moustafa, S. El-Taher, M. F. Shbil, and R. Hilal, *Int. J. Quant.Chem.*, **87,** 378 (2002).

[23] R. Hilal and H. Moustafa, *Int. J. of Quantum Chem.*, **25,** 183 (1984).

[24] Mathcad 7.0 (professional edition) from Mathsoft Co. U.K., 1986–1997.