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Theoretical study of the excited state intramolecular proton transfer in barbituric acid

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Abstract

AM1 calculations on the tautomers of barbituric acid have been carried out for the singlet and triplet states of these molecules. The results show that the triketo form, which is most stable for the ground state, gets destabilized on excitation, as the cleavage of a carbon–nitrogen bond occurs. Large changes in geometry on excitation are confined mainly to the urea portion of the molecule and the carbonyl groups. This has been explained from an analysis of the highest occupied and lowest unoccupied molecular orbitals. The absorption and fluorescence spectra have also been calculated, and these indicate that absorption takes the ground state triketo form of the molecule to its ($\pi\pi^*$) excited state, which may easily isomerize to the 4-hydroxy form, which has a more stable singlet excited state. Fluorescence then occurs from this state. This is especially likely since the proton transfer barrier reduces substantially for the excited state.

Keywords: Barbituric acid; Singlet; Triplet; Excited state proton transfer; Absorption and fluorescence spectra; Tautomerism

1. Introduction

The investigation of excited electronic states is essential for determining the possibility of using various organic compounds having nearby proton donor and acceptor sites as photostabilizers. Several such molecules undergo protomeric shifts in some excited electronic states. Excited state proton transfers (ESPT) also play a significant role in several biological processes.

We have seen previously [1] that barbituric acid displays keto-enol tautomerism, the most important tautomers being the triketo form (**I**, see Fig. 1) and the 4-hydroxy tautomer (**II**) obtained from **I** by proton transfer from the methylene carbon to a keto oxygen. However, the barriers to the proton transfer are quite high, though solvation with water brings down the barriers considerably.

We now report calculations on the first excited singlet and triplet states of barbituric acid, and the effect of excitation on the tautomerization energies and activation barriers.

2. Computational details

The investigation of potential energy surfaces for excited electronic states, with sophisticated ab initio configuration interaction (CI) or multiconfigurational schemes, is impractical, especially since accurate ab initio computations of hydrogen bond energetics require large polarized basis sets [2] and BSSE corrections [3]. Semi-empirical methods being the next choice, the reliability of the chosen procedures must be critically judged with special reference to systems

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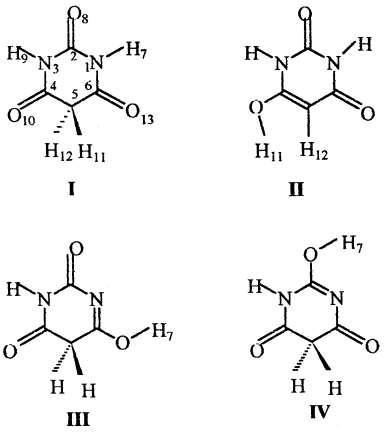

Fig. 1. Molecular structures of barbituric acid tautomers.

and processes as close as possible to those to be investigated.

The AM1 [4–6] semi-empirical method, a modification of MNDO [7], offers more accurate parameterization than MNDO for polar systems and transition states. It yields reliable results for ground state geometries, heats of formation, and relative stabilities of tautomeric species [8]. For the excited states too, the quality of the AM1 approximation seems acceptable [9–18]. Good results have been reported concerning the dynamics of some photochemical processes [15,16] and conformational changes induced in polyenes by photoexcitation [10,17,18]. Ertl [10] has pointed out that AM1 yields geometrical parameters for excited states in good agreement with experiment, its only drawback being a slight underestimation of transition energies. In view of this, we have based our calculations on the AM1 Hamiltonian, which has been found to reproduce experimental data for ground states [1] fairly accurately.

Table 1
Heats of formation (kJ/mol) of the barbituric acid tautomers after CI interaction (see Fig. 1)

System	Heats of formation		
	S_0	S_1	T_1
I	− 460.3	− 26.4	− 86.1
II	− 417.1	− 93.3	− 218.6
III	− 403.2	− 83.8	− 136.6
IV	− 374.0	− 79.4	− 93.1
TS1	− 131.1	54.1	38.2

CI calculations further refined the ground state (S_0) calculations, initially done at the closed-shell Hartree–Fock (HF) single-determinant SCF level [1]. However, there is negligible improvement in the ground state energies. The CI subspace included 100 lowest energy configurations obtained by single and double electron excitations from the three highest occupied (HOMO − 2) to the lowest three empty molecular orbitals (LUMO + 2) [19]. The use of these microstates in the CI calculation provides a fair representation of correlation effects. The lowest root in the CI calculation corresponds to the ground state (S_0), while the first excited root refers to the S_1 state. Complete geometry optimization without constraint has been carried out for the lowest and the first excited roots. It may be mentioned that, for the excited states, it was not possible to obtain very low gradient values, as in the SCF calculations. Since there are several orbitals in a small energy range, extensive CI was carried out at these geometries, including all degenerate or nearly degenerate orbitals. In fact, all orbitals within 10 eV of the HOMO and LUMO were taken for the CI calculation, ensuring that all n and π orbitals were included.

Transition energies for absorption were calculated at the ground state optimized geometry, and the fluorescence spectra were computed at the excited state geometry.

For the lowest triplet state (T_1), calculations were performed using the open-shell restricted Hartree–Fock (RHF) methods at the SCF level. The unrestricted Hartree–Fock (UHF) method was avoided, though, in general, UHF methods yield lower energies with respect to RHF calculations [20]. This was done to avoid spin contamination by states of other multiplicities, which may increase the tendency of the geometrical symmetry of the molecule being destroyed during the geometry optimization.

All calculations were performed with the MOPAC 7.0 program package [21].

3. Results and discussion

3.1. The S_0 and S_1 electronic states of barbituric acid

3.1.1. Relative energies

The CI results for the ground (S_0) state of barbituric

Table 2
Optimized geometries of barbituric acid (**I**) after configuration interaction (bond lengths in Å and angles in degrees)

Bond parameter[a]	S_0	S_1	T_1
C_2N_1	1.406	2.029	1.524
N_3C_2	1.406	1.367	1.398
C_4N_3	1.394	1.384	1.390
C_5N_4	1.508	1.514	1.514
C_6N_1	1.394	1.407	1.456
C_6C_5	1.508	1.503	1.502
H_7N_1	0.999	1.991	1.014
O_8C_2	1.246	1.206	1.241
H_9N_3	0.999	1.001	0.999
$O_{10}C_4$	1.240	1.246	1.244
$H_{11}C_5$	1.126	1.134	1.126
$H_{12}C_5$	1.126	1.129	1.127
$O_{13}C_6$	1.240	1.241	1.236
$N_3C_2N_1$	118.8	114.7	118.0
$C_4N_3C_2$	123.5	123.6	124.0
$C_5C_4N_3$	118.9	124.8	120.7
$C_6C_5C_4$	116.4	123.8	118.2
$H_7N_1C_2$	116.9	133.0	119.6
$O_8C_2N_3$	120.6	135.9	119.6
$H_9N_3C_2$	116.9	118.8	118.2
$O_{10}C_4N_3$	119.3	117.3	119.2
$H_{11}C_5C_4$	108.2	105.6	107.3
$H_{12}C_5C_4$	108.2	106.8	107.2
$O_{13}C_6C_5$	121.8	119.1	121.2
$C_4N_3C_2N_1$	0.0	0.1	0.2
$C_5C_4N_3C_2$	0.0	0.0	− 0.2
$C_6C_5C_4N_3$	0.0	0.0	0.2
$H_7N_1C_2N_3$	180.0	− 179.6	179.7
$O_8C_2N_3C_4$	180.0	− 179.4	179.6
$H_9N_3C_2N_1$	180.0	179.1	180.0
$O_{10}C_4N_3C_2$	180.0	− 179.3	179.8
$H_{11}C_5C_4N_3$	122.0	− 123.9	− 122.6
$H_{12}C_5C_4N_3$	122.1	122.4	122.8
$O_{13}C_6C_5C_4$	180.0	179.1	179.9

[a] See Fig. 1.

acid were first compared with the SCF calculations performed earlier [1], and the heats of formation are given in Table 1. Comparison of the optimized geometry for the ground state triketo form (**I**) of barbituric acid (Fig. 1), obtained after inclusion of CI, with the corresponding SCF values shows that there is only a marginal difference in the two results. Hence, although CI calculations reduce the optimized energies by a few kJ/mol, no significant changes in the geometries are found. For all the four tautomers, the ground state configuration contributes more than 98% to the final CI result. The computations at the CI level

Table 3
Calculated singlet–singlet transition energies in electron volts and the weightage of the most important microstate (HOMO = MO#33) in the excited state

System	ΔE	%	Transition
Absorption			
I	5.68		
II	4.26	92.2	33 → 35
III	4.80		
IV	4.07	94.5	32 → 34
Fluorescence			
I	0.02	99.1	34 → 33
II	2.14	87.8	34 → 33
III	1.07	89.3	34 → 33
IV	1.85	98.8	34 → 33

again indicate the triketo form of barbituric acid as the most stable tautomer in the ground state, and it is more stable than the next (4-hydroxy, **II**) tautomer by 43 kJ/mol. The activation energies for the tautomerization reactions were found to be very high [22] (~310 kJ/mol), and this rules out a direct proton transfer mechanism in the ground electronic state.

The first excited singlet states (S_1) for the four important tautomeric forms, viz. **I**–**IV** (Fig. 1), were also investigated, and the results are given in Table 1. The first thing that strikes about the results is that the 4-hydroxy form (**II**) is stabilized to the greatest extent. Therefore, in the excited state, this becomes the most important form (Table 1), being more stable than the triketo form by 67 kJ/mol. In fact, all the tautomeric forms become more stable than the triketo form in the excited state.

3.1.2. Molecular structures

Table 2 compares the computed geometrical parameters for barbituric acid in the S_0 and S_1 electronic states. One can see that drastic changes occur in the upper half of the barbituric acid ring on excitation. In particular, the most significant of these is an increase in the C_2–N_1 bond length (Fig. 1), abolishing the C_{2v} symmetry of the molecule. This bond almost breaks on excitation. Large changes occur for the other tautomers too, but there is no breaking of the carbon–nitrogen bonds. Changes also occur in the carbonyl bond lengths, especially in the S_1 state of **III**, for which the C_2=O_8 bond length increases, and both the excited states of **IV**, in which the C_6=O_{13} bond length

increases. The changes in the upper half of the ring are expected, as the HOMO of barbituric acid is concentrated in this, the urea part, of the ring. The LUMO, however, involves the carbonyl bonds, and so HOMO–LUMO excitations lead to changes in these too.

3.1.3. Electronic states and UV spectra

The transition energies computed for the absorption spectra of the different systems are reported in Table 3. The energy values refer to vertical transitions from the optimized geometry of the ground states. The calculated absorption wavelength for **I** (218 nm) is in excellent agreement with the observed value of 212 nm [23,24]. Solvent studies indicate that this band arises from a ($\pi\pi^*$) transition [25]. This is in agreement with conclusions drawn from our calculated results [1]. It was observed that barbituric acid (along with its tautomeric forms) is characterized by high values of the ionization potential and electron affinity. Naturally, the large HOMO–LUMO gap implies short wavelength absorption. The HOMO and LUMO in barbituric acid were found to be, respectively, the carbonyl π and π^* orbitals. However, since there are three nearly degenerate highest occupied levels, two of which (HOMO, HOMO − 2) are of the π type, and the third (HOMO − 1) is of the oxygen nonbonding type, CI leads to a mixing of these levels. Between the ground state and the excited singlet, there are three triplet states at 4.62, 4.89 and 5.52 eV above the ground state singlet. It is found that in the hydroxy tautomers of barbituric acid, the transition energies are smaller than for the triketo form (Table 3).

The electronic origin of these effects is quite apparent on inspection of the energies and natures of the frontier orbitals of the important tautomers. The HOMOs of the tautomers are very different from one another. For **I**, the HOMO corresponds to the nitrogen lone pairs and the out-of-plane orbital on O_8, while for **II**, it is mainly localized at C_5. The HOMO energy of **II** is lower by about 1.7 eV than that of **I** due to a stronger bonding interaction. The LUMOs are dominated by antibonding carbonyl interactions. However, small bonding C_4–C_5 interactions are only operative in **II**. These lower the LUMO energy of the 4-hydroxy form (**II**) by ~0.1 eV versus that of the lactam form. Thus, if one neglects electron repulsion, for **II**, there is a net decrease in the HOMO–LUMO gap, which decreases the excitation energy. These effects also explain the stabilization of **II** with respect to **I** upon electron excitation from S_0 to S_1. The electrostatic term too favors the form with the higher dipole moment, which is the 4-hydroxy (**II**) tautomer (3.91 D, as compared with 0.68 D for the triketo form) in this case.

In Table 3, we also show the computed transition energies for the fluorescence spectra. The energies refer to vertical transitions from the optimized geometry for the first excited singlet state. The emission wavelengths for all tautomers are red-shifted with respect to the corresponding absorption wavelengths. This behavior, when observed in other similar systems, like the 2-pyridone-2-hydroxypyridine system, is generally interpreted in terms of direct intramolecular proton transfer in the excited electronic state [26–30]. However, these results show that this effect is due to other reasons, and is, instead, connected to the strong deformations of bond distances in the ring upon electronic excitation. In the triketo form, the changes involve mainly the upper portion of the ring, the most important being the increase of the C_2–N_1 distance and the decrease of the C_2=O_8 bond length. For the tautomers, the changes are less dramatic, but involve all the C–C bonds in the ring, Cline-Love and Upton [31] found microsecond lifetimes for 5,5-disubstituted barbiturates. This suggests that the fluorescence transition is of the ($n\pi^*$) type, although the absorption should be of the ($\pi\pi^*$) type.

No fluorescence should be seen from barbituric acid (**I**), as excitation would lead to carbon–nitrogen bond cleavage. Furthermore, the large red shift (about 290 nm at the AM1 level) between the absorption and fluorescence spectra of **II** is strongly related to the very different structure of the HOMO and LUMO orbitals. The difference is reflected in the molecular geometry. For this tautomer, HOMO–LUMO excitation shifts the electron density from C_5 to C_4, and this increases the C_4–C_5 bond length on excitation.

The opening of the barbituric acid ring on photolysis has been experimentally observed. Otsuji et al. [32] found that the hydrolysis of 5,5-diethylbarbituric acid, in alkaline solution, is accelerated by UV (254 nm) light. It was also found that the photochemical ring opening occurs at the side other than that

found in the hydrolytic pathway (i.e. N_1–C_2 instead of N_1–C_6).

3.1.4. Electronic effects

This simple scheme is further supported by considerations based on the computed bond orders and net atomic charges, based on the Mulliken population analysis. The most important changes produced in the triketo form (**I**) by excitation are the significant increase in the bond order of the C_2=O_8 carbonyl bond (from 1.751 to 1.912), and the corresponding decrease in the bond orders for the other carbonyl bonds. Modifications also occur in the other tautomers, and these involve almost all the bonds, the largest changes involving the ring bond orders. In particular, the N_3–C_2 bond order decreases substantially for **II**.

Some polar organic molecules, most notably the oxazines, exhibit significant shifts in electronic charge at their heteroatom sites on excitation, giving rise to state-dependent dynamical properties [33–37]. Barbituric acid should also exhibit this characteristic. Comparison of the calculated results for the S_0 and S_1 state charge distributions for the triketo tautomer (**I**) shows that there is a state-dependence to the charges on the heterocyclic nitrogens and keto oxygens. We note that, on excitation, the nitrogen (N_1) becomes more positive by $\sim$0.29*e*, but there appears to be no significant corresponding negative charge accumulation at the keto oxygens. Rather, there is a flow of electron density from the heteroatoms to the electron deficient carbons, particularly C_2 and C_6, and the hydrogens in the excited state. Excitation is also accompanied by an increase in the dipole moments of the **I** (m = 0.44, 1.06 and 1.68 D, respectively, for the S_0, S_1 and T_1 states, respectively) and **II** forms, but a decrease in the dipole moments for the **III** and **IV** forms is predicted.

Observed changes in the energetics and topographies accompanying $S_1 \leftarrow S_0$ excitation can be qualitatively understood from the nature of the frontier orbitals of barbituric acid. The HOMO and LUMO are both composed of the out-of-plane π orbitals. The participation of the nitrogens is very large in the HOMO, but the reverse is true for its participation in the LUMO, i.e. HOMO $\rightarrow$ LUMO excitation provides a mechanism for electron density to flow from the nitrogens to the carbonyl carbons. From a conventional point of view, the nitrogens become less electron-rich (less basic) and proton transfer from them becomes easier in the excited state.

The excited states are seen to be diradicals. In the S_1 electronic state of barbituric acid (**I**), one electron is located mainly at N_1 (75%), and C_2 (47%) and O_8 (18%) share the other. This explains the increase in the C_2–C_8 bond order upon excitation. However, in **II**, there is greater delocalization of the electron in the higher energy orbital, which is spread over the entire ring. The lower energy orbital contains an unpaired electron at C_5. In **III**, the lower energy electron is at O_8, while the other is distributed between C_2 and C_4. In **IV**, the distribution is, respectively, at O_{13} and C_2 and C_6. Thus, in the latter two cases, involving proton transfers from nitrogens, one electron is localized at carbonyl oxygen, and the other is shared between two opposite carbons. This also explains the increase in the corresponding bond lengths and the increase in their bond orders.

3.2. The triplet (T_1) state

The heats of formation of the barbituric acid tautomers in the T_1 state, calculated with the open-shell restricted Hartree–Fock (RHF) method, followed by CI, are given in Table 1, and the fully optimized topographic parameters for the triketo form are given in Table 2. A close look into the values displayed shows that the predicted changes in the geometrical parameters in the T_1 states parallel what has been observed in the corresponding S_1 states. From Table 1, it is seen that the 4-hydroxy tautomer (**II**) is again stabilized most, and is more stable than the triketo form by 133 kJ/mol. Thus, excitation reverses the order of stabilities between the two tautomers. In fact, **I** becomes the least stable of all the tautomers.

The bond orders and the charge densities exactly parallel the trends observed for the excited singlets. The triplet state is formed by an essentially HOMO–LUMO excitation. This configuration accounts for 99.8% of the excited triplet for barbituric acid. For the 4-hydroxy tautomer (**II**), this term has a slightly smaller contribution (98.5%), while for **III** and **IV**, its contributions are 96.7 and 97.9%, respectively.

In this case too, the barbituric acid diradical constitutes one electron on N_1; the higher energy singly occupied orbital, however, contains an electron distributed over the entire molecule, including N_1.

As expected, the unpaired electron spin density is concentrated at N_1 (1.489), showing that the C_2–N_1 bond breaking occurs with both electrons of the bond going to the nitrogen, one in the 2s orbital, and the other in the $2p_z$ orbital of the nitrogen. In **II**, the unpaired spin density is distributed over the carbons, while in **III** and **IV**, the spin densities are maximum at oxygens O_{10} and O_{13}, respectively.

3.3. Proton transfer kinetics in the excited singlet (S_1) and triplet (T_1) states

Since the relative tautomer energies differ in the excited electronic states, it is pertinent to examine the activation barriers to the proton transfers in the excited states. The tautomerization reactions from the triketo form are endothermic in the ground state, but become exothermic in the excited states. ESPT therefore becomes a possibility if the proton transfer barrier is also not too high. The calculated activation barrier (see Table 1) for the S_0 electronic state (329 kJ/mol) is found to be four-fold higher than that for the S_1 state (81 kJ/mol) and it may be surmised that proton transfer is possible in the S_1 electronic state because of the low activation energy. The geometries of the transition states for proton transfers are similar for the three electronic states investigated. For the triplet state too, the proton transfer barrier (124 kJ/mol) is much lower than that for the S_0 state, although it is not as low as that for the S_1 state.

4. Conclusions

Our calculations lead us to the following conclusions:

1. The singlet and triplet excited states are similar in structure.
2. Excitation leads to a destabilization of the ground state stable tautomer (**I**) and the tautomer (**II**) becomes the most stable. This is because cleavage of a C–N bond should take place for **I**.
3. The excited state is a ($\pi\pi^*$) state. Excitation is accompanied by a flow of electron density from the nitrogens to the carbon atoms of the ring.
4. Excitation also considerably decreases the proton transfer activation barriers, and excited state proton transfer becomes a distinct possibility for this molecule. A ($\pi\pi^*$) excitation takes the molecule to the S_1 state of **I**, which may undergo tautomerization to **II**, since the activation barrier is not too high, and fluorescence takes place from the S_1 state of **II**.

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