

Spectroscopic Analysis of Tautomeric Forms of 5-Phenyltetrazole*

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Experimental and theoretical directions of electronic transition moments and the UV spectra of anionic and neutral 5-phenyltetrazole (5-PhTH) have been determined. Based on the correlation between the theoretical and experimental data it has been found that the 2-H-tautomeric form is predominant in polyvinyl alcohol (PVA) film.

1. Introduction

The phenomenon of tautomerism plays an important role in chemistry and biology. 5-phenyltetrazole (5-PhTH) and its derivatives belong to the group of chemical compounds which exhibit tautomerism. The tautomeric equilibria involving this compound have been studied by many investigators [1–19] but the results reported are still doubtful. This is due to the fact that the difference between the tautomeric forms consists only in the position of the proton in the tetrazole ring. The physicochemical properties of these tautomers are therefore almost the same. On the other hand, the position of the proton is responsible for the value of the electric dipole moment and the direction of the electronic transition moment, parameters which are readily accessible by quantum mechanical calculations. Therefore, the experimental determination of these parameters and their comparison with the theoretical values can enable the tautomeric equilibrium to be analyzed, deciding which of the tautomers is predominant.

2. Experimental

2.1. Samples and Methods

5-PhTH was synthesized and purified as described elsewhere [6]. Polyvinyl alcohol (PVA) films were prepared using a technique resembling that employed by

Tanizaki [20]. The PVA films were five-fold stretched at about 350 K, the rate of stretching being controlled. For the measurements, films were selected which displayed the least heterogeneities. Since 5-PhTH is a relatively strong acid (its dissociation constant being 1.05×10^{-5} in 50% ethanol [6]), in the PVA environment with pH of about 6 it occurs mainly in the anionic form. The undissociated form was obtained by acidifying the aqueous solution of tetrazole in PVA with $0.1 \text{ N H}_2\text{SO}_4$, after which the pH of the film amounted to about 3. It has been proved that at this pH the plastic properties of the film do not change. Such a procedure enables to obtain high concentrations of the compound investigated in the film (about 10^{-2} M), contrary to the method of diffusion of a compound from acidic solution to a PVA film [21, 22]. The method of acidifying the 5-PhTH solution in H_2SO_4 thus enables the weak absorption band at 35.5 kK to be investigated.

Polarized absorption spectra were measured by means of an apparatus described in [23].

2.2. Basic Equations of the Analysis of Linear Dichroism

For the analysis of the polarized spectra different models were used. The general Matsuoka and Norden [24] equation for the reduced linear dichroism (LD^r) as a function of the orientation parameter S_{ii} ($i = x, y, z$) and the angle α between the long molecular axis and the transition moment vector (cf. Fig. 2), can be expressed in the diagonal reference system by the formulae

$$\text{LD}^r = 3(S_{yy} \sin^2 \alpha + S_{zz} \cos^2 \alpha), \quad (1)$$

$$\frac{\text{LD}^r}{3} = K = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}} = \frac{R_d - 1}{R_d + 2}. \quad (2)$$

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K is the absorption anisotropy [23], A_{\parallel} and A_{\perp} are the components of the absorbance ($A = \varepsilon C l$, where ε is the molar absorption coefficient in litres per mol · cm, C the concentration in mol/l, and l the length in cm) parallel and perpendicular to the distinguished stretching direction of the film (e.g. the z -axis), and

$$R_d = A_{\parallel}/A_{\perp} \quad (3)$$

the measured dichroic ratio.

Norden's orientation parameters S_{ii} [25] are unequivocally related to parameters K_i proposed by the TEM model [26–28]:

$$S_{ii} = \frac{3}{2} K_i - \frac{1}{2}. \quad (4)$$

$$D = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} = \frac{R_d - 1}{R_d + 1} = \frac{(3A - 1) \{ [3C(1 - B) - 1] + 3C(2B - 1) \cos^2 \alpha \}}{(3 - A) + C(3A - 1)(1 - B) + C(3A - 1)(2B - 1) \cos^2 \alpha}. \quad (7)$$

A simple reducing procedure for the TEM model [26–28] was employed to determine the orientation parameters K_i . For molecules of high symmetry (C_{2v}), the observed components of the absorption spectra (parallel A_{\parallel} and perpendicular A_{\perp}) are a linear combination of pure polarized transitions along the y - and z -axes. For the overlapping absorption bands, when creating the linear combination of the spectral components, $A_{\parallel}(\tilde{\nu}) - d_i \cdot A_{\perp}(\tilde{\nu})$, the value of d_i corresponding to a separated i -th transition can be readily determined [29]. The orientation parameters can be obtained by this method:

$$K_i = d_i / (2 + d_i). \quad (5)$$

The orientation parameters thus determined for the 5-PhTH anion amount to $K_z = 0.603$ and $K_y = 0.31$. Using such orientation parameters and employing (1) and (4), the angle α between the transition moment direction and the long molecular axis can be found.

The analysis of the dichroism spectra was also carried out by employing the semi-empirical Popov model [30–32]. The respective orientation parameters are in this model related for the molecular shape. For the neutral molecules and the 5-PhTH anion, the parameter C based on the calculated length of the molecule amounts to 0.9 [31]. For the anion 5-PhTH, the parameter B can be calculated from the dichroism spectra for the short-wave absorption band polarized

along the long molecular axis by use of the equation [31]

$$B = \frac{(3A - 1) + (3 - A)D_{\parallel}}{C(3A - 1)(3 - D_{\parallel})}, \quad D_{\parallel} = \frac{R_d^{\max} - 1}{R_d^{\max} + 1}, \quad (6)$$

where R_d^{\max} denotes the mean maximum dichroic ratio (cf. (3)) measured in the short-wave region of the absorption band. For five-fold stretched PVA films, $A = 1$ [30–32].

For a measured value of $R_d^{\max} = 3.03$ (Fig. 1 a) we obtain from (6): $D_{\parallel} = 0.504$ and $B = 0.66$. This value of B is in good agreement with that determined from the geometrical analysis of the shape [31]. Popov [31] obtained the following general expression for dichroism:

The angles α obtained from (1) and (7) are given in Table 2.

3. Quantum Mechanical Calculations

The absorption spectra were calculated by the CNDO/S-Cl method with the original parametrization of DelBene and Jaffe [33]. The electrostatic nPDQ model [34] (n point dipoles and quadrupoles) was used to determine the influence of the environment on the position of the absorption bands. The electrostatic field produced by the solvent molecules according to this model can be used for the calculation of the solvation energy of the ground state in the CNDO/S method [35]. Obviously, this is only the electrostatic part of the energy of the interaction between the solute and the solvent molecules. Nevertheless, it is sufficient for a qualitative description of the solvation phenomenon. The same geometry of the tetrazole ring as in our previous paper [9] was used in the calculations. The geometry of the phenyl ring has been calculated using the standard values of the bond lengths and angles. The length of the bond linking these two rings has been optimized with the MNDO method and found to be 1.43 Å. Thirty singly excited configurations were used in the CI method.

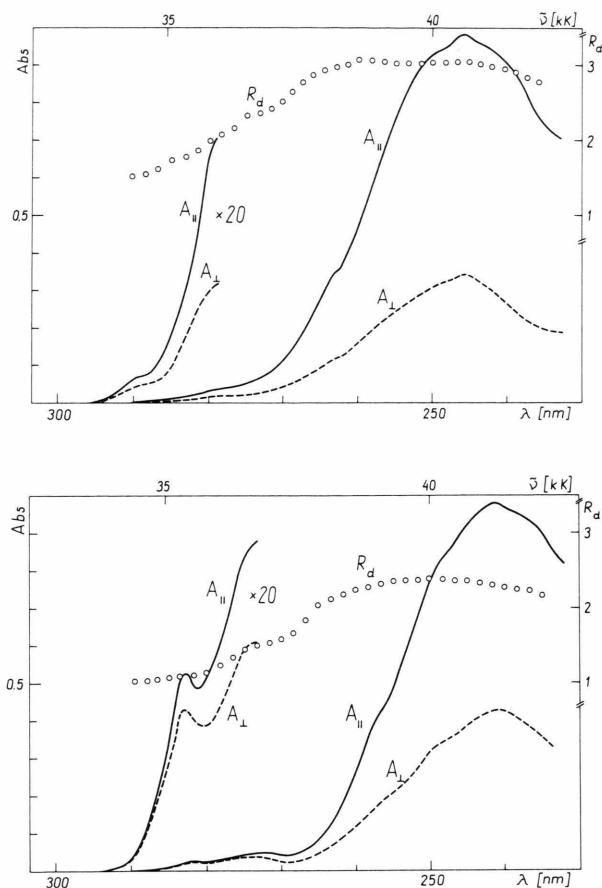


Fig. 1. Parallel ($A_{||}$) and perpendicular (A_{\perp}) components of absorption and dichroic ratio R_d vs wavelength λ of the anion (Fig. 1a) and undissociated molecule (Fig. 1b) of 5-PhTH in five-fold stretched films.

The tautomeric equilibrium constant, $K_{1,2}$, can be expressed by the equation

$$K_{1,2} = \exp(-\Delta E_{1,2}^y/kT), \quad (8)$$

where $\Delta E_{1,2}^y$ is the difference between the microscopic energies of the ground states of two tautomers, the values of which can be calculated by quantum-mechanical methods. If $\Delta E_{1,2}^y < 0$, then the 1H-tautomer has the lower energy, and vice versa. Therefore the difference in energy is sufficient to determine which of the tautomeric forms of 5-PhTH will be predominant in the gas phase. The change in the ground state energy of a given tautomer when passing from gas phase to solution can be expressed by

$$\delta \mathcal{E}_{1H} = E_{1H}(S_0, s) - E_{1H}(S_0, v), \quad (9)$$

where $E_{1H}(S_0, s)$ is the ground state energy of the 1H-tautomer in the solution and $E_{1H}(S_0, v)$ in the gas phase. Similarly, for the excited states we can write

$$\delta \mathcal{E}_{1H}^{*(i)} = E_{1H}(S_i, s) - E_{1H}(S_i, v), \quad (10)$$

where S_i denotes the i -th excited state. The relative change in the ground state energy resulting from the influence of the environment is given by

$$\Delta \mathcal{E}_{1H, 2H} = \delta \mathcal{E}_{1H} - \delta \mathcal{E}_{2H}, \quad (11)$$

and for the excited states by [34]

$$\Delta \mathcal{E}_{1H, 2H}^* = \delta \mathcal{E}_{1H}^* - \delta \mathcal{E}_{2H}^* \quad (12)$$

$$\begin{aligned} \Delta \mathcal{E}_{1H, 2H}^* &= \Delta \mathcal{E}_{1H, 2H} + hc(\Delta \tilde{\nu}_1 - \Delta \tilde{\nu}_2) \\ &= \Delta \mathcal{E}_{1H, 2H} + hc[\Delta \tilde{\nu}_{1,2}(v) - \Delta \tilde{\nu}_{1,2}(s)], \end{aligned} \quad (13)$$

where $\Delta \tilde{\nu}_1 = \tilde{\nu}_1(v) - \tilde{\nu}_1(s)$ and $\Delta \tilde{\nu}_2 = \tilde{\nu}_2(v) - \tilde{\nu}_2(s)$ denote the changes in the transition wavenumbers of the 1H- and 2H-tautomer, respectively, when passing from the gas phase (v) to the solution (s). Certainly, the solvent affects also the values and directions of the transition moments.

4. Results and Discussion

The results of the calculations carried out for both tautomeric forms and the anion of 5-PhTH are summarized in Table 1 (for transitions $S_0 \rightarrow S_i$, $i = 1 \div 5$). Based on (9), we calculated the energies of stabilization of the tautomeric forms of 5-PhTH by water molecules within the 3PDQ model. They were found to be 35 kcal/mol for the 1H-tautomer (average per one point dipole-quadrupole amounting to 11.6 kcal/mol) and 41 kcal/mol for the 2H-tautomer (average 13.6 kcal/mol). Considering the fact that in the gas phase the 2H-tautomer has a lower energy than the 1H-tautomer, and that it is better stabilized by the water molecules, it can be presupposed that the 2H-tautomer dominates in the ground state in aqueous solution. The difference between the hydration energies of the tautomers is $\Delta \mathcal{E}_{1H, 2H} = 6$ kcal/mol to the advantage of the 2H-form. The calculated hydration energy for the anion of 5-PhTH in the 4PDQ model is 51 kcal/mol (12.7 kcal/mol average for one point dipole-quadrupole). Analysing the results given in Table 1 it can be observed that hydration of the 1H-tautomer does not cause a great change in the electronic spectra. On the other hand, hydration causes significant changes in the evaluated spectrum

Table 1. Characteristics of electronic transitions of 5-PhTH in gas phase (CNDO/S CI) and in solution (nPDQ) (* Oscillator strength).

Compound	Transition	Gas phase			Solution			$\Delta\mathcal{E}$
		ΔE [kK]	f^*	Polarization	ΔE [kK]	f^*	Polarization	
1 H-tautomer of 5-PhTH	$S_0 \rightarrow S_1$	36.9	0.0017	6°	36.5	0.0133	58°	(–)
	$S_0 \rightarrow S_2$	39.9	0.3737	2.5°	39.5	0.3498	2.5°	(–)
	$S_0 \rightarrow S_3$	40.6	0		40.3	0		(–)
	$S_0 \rightarrow S_4$	44.4	0		45.5	0		(+)
	$S_0 \rightarrow S_5$	48.8	0		48.1	0.0741	15°	(–)
2 H-tautomer of 5-PhTH	$S_0 \rightarrow S_1$	36.1	0		35.9	0.0075	84°	(–)
	$S_0 \rightarrow S_2$	37.1	0		35.9	0		(–)
	$S_0 \rightarrow S_3$	41.1	0		39.7	0.3066	11°	(–)
	$S_0 \rightarrow S_4$	41.6	0.2885	13°	41.1	0		(–)
	$S_0 \rightarrow S_5$	44.4	0.0398	30°	43.3	0.0241	63°	(–)
Anion of 5-PhTH	$S_0 \rightarrow S_1$	32.3	0		36.1	0		(+)
	$S_0 \rightarrow S_2$	33.7	0.0025	83°	36.4	0.0051	78°	(+)
	$S_0 \rightarrow S_3$	35.2	0.3180		37.3	0.2410		(+)
	$S_0 \rightarrow S_4$	36.7	0		37.5	0		(+)
	$S_0 \rightarrow S_5$	37.9	0.9970	89°	42.0	0.0036	87°	(+)

Table 2. Theoretical and experimental values of polarization angles of electronic transition moments (in deg.)

	Theoretical				Experimental	
	α		$\alpha' = (\alpha \pm \gamma)$		α	α
	1 H-tautomer	2 H-tautomer	1 H-tautomer	2 H-tautomer	TEM model (1)	Popov model (7)
I transition	58	84	68	74	70.0	69.5
II transition	2.5	11	7.5	21	25.0	24.5

with simultaneous inversion of states, which makes the spectrum of the 2H-tautomer very similar to the spectrum of 1H-tautomer for $\pi_0 \rightarrow \pi_i^*$ transitions. Apart from this, it should be noted that the spectrum of the 5-PhTH anion in the gas phase differs from those of the 1H- and 2H-tautomers, that the hydration, however, makes them very similar, in particular for $\pi_0 \rightarrow \pi_i^*$ transitions. Due to these facts, a straightforward interpretation of the experimental spectra in order to establish the tautomeric equilibrium for 5-PhTH in solution is impossible.

Analysing the results shown in Table 1 ($\pi_0 \rightarrow \pi_i^*$ transitions) it can be inferred that the three forms studied have different values of electronic transition moments. In Figs. 1a and 1b, the experimental absorption spectra are presented in the UV range for both components, parallel A_{\parallel} and perpendicular A_{\perp} , as well as the value of the dichroic ratio $R_d = A_{\parallel}/A_{\perp}$, measured in five-fold stretched PVA films for the an-

ionic and neutral forms of 5-PhTH. It can be observed that the neutral and anionic forms differ in the values of dichroism. For the anionic form it ranges from 1.52 (minimum) to 3.03 (maximum), while for the neutral form the values amount to 1.05 (minimum) and 2.44 (maximum). It is worth noticing that the measured spectra in methanol and in the isotropic PVA system are almost the same. Based on the spectra obtained, it seems that the short-wave absorption band (41 kK) of both the anionic and neutral molecule is a transition of pure polarization, occurring along the C_{2v} symmetry axis. The long-wave absorption band (35.5 kK) lying in the background of the short-wave band is a band of weak oscillator strength (f). The transition from the anionic form of pure C_{2v} symmetry to the neutral molecule changes the position of the long axis by a small angle γ (Figure 2). As is well known [21, 22, 24, 34–38], the changes in the position of the long axis (orientation axis) accompanied with gaining

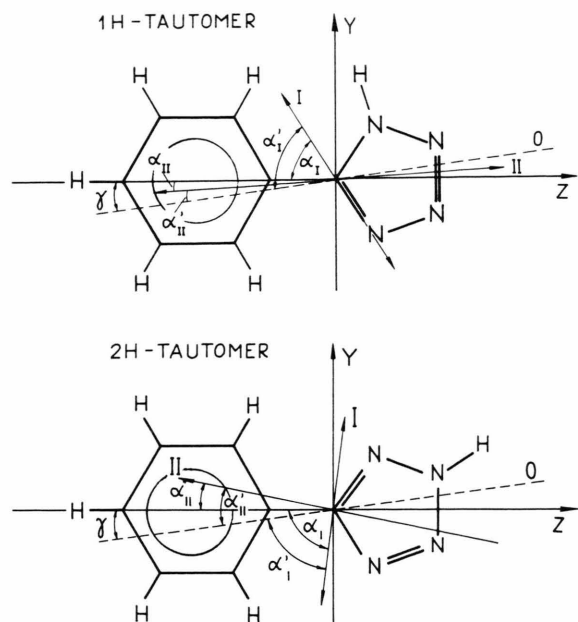


Fig. 2. 1H-tautomer (Fig. 2a) and 2H-tautomer (Fig. 2b) of 5-PhTH. Denotations: α_I and α_{II} calculated angles between the direction of the long wave (α_I) and short wave (α_{II}) electronic transitions, respectively, and the Z axis of the molecule. α'_I and α'_{II} angles of these transitions with respect to the assumed orientation axis 0. γ is the angle between the axis 0 and the axis Z.

or losing the proton are very slight. As a consequence, the orientation parameters are approximately the same for the anion and the neutral molecule. Therefore, the orientation parameters were determined for the anionic form, and the same values were assumed for the neutral molecule. Figure 2 shows the tautomers with

theoretically calculated directions of the electronic transition moments (α_I , α_{II}) and the values of α'_I and α'_{II} , modified by the angle γ .

Taking into account the small change of the orientation axis of the molecule compared with the orientation of the anion in the PVA film (angle γ), a correlation can be established between the theoretical and experimental values of the directions of the electronic transition moments. Assuming the γ to be small ranging from 0° to 15° , the theoretical value of α can be estimated for both absorption bands (see Fig. 2):

$$\text{for 1 H-tautomer } \alpha'_I = \alpha_I + \gamma \quad \text{I transition (36.5 kK)}$$

$$\alpha'_{II} = \alpha_{II} - \gamma \quad \text{II transition (39.5 kK)}$$

$$\text{for 2 H-tautomer } \alpha'_I = \alpha_I - \gamma \quad \text{I transition (35.9 kK)}$$

$$\alpha'_{II} = \alpha_{II} + \gamma \quad \text{II transition (39.7 kK)}$$

The data presented in Table 2 show that there is good agreement between the theoretical and experimental values of the direction of the electronic transitions. It should also be noted that varying the value of γ causes no qualitative change of the results. On the other hand, it has been shown that the solvent effect must be included in the calculations to get properly the direction of the shift of the band positions and the direction of the electronic transition moments. Based on the correlation between the theoretical and experimental values of the angle α it can be established which of the tautomers is predominant. In our case, such a combination of calculations and measurements carried out in an ordered system (PVA film) has unambiguously revealed that the dominating form is the 2H-tautomer of 5-PhTH.

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