Electronic Spectra of Cyano-5-phenyltetrazoles

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Absorption and luminescence spectra of *ortho-*, *meta-* and *para*-cyano-5-phenyltetrazole in aqueous solutions at room and low temperature were measured. Investigations were carried out in super acidic ($H_o = -8$) to basic (pH = 12) media. Three dissociation forms were identified (anion, molecule and cation), and the corresponding acid-base equilibrium constants in the ground state, spectrophotometrically, and in the first excited singlet state from the titration curves and by Förster cycle were determined.

INTRODUCTION

The values of the thermodynamic dissociation constants (molecule-anion equilibrium) were determined by the potentiometric method for *ortho-* and *para*-cyano-5-phenyltetrazole in 50% ethanol-water and for *meta*-cyano-5-phenyltetrazole in 75% dimethylsulphoxide-water mixture.[1] Recently,[2,3] the absorption (mainly the longwave band $S_o \rightarrow S_1$) and luminescence spectra of these compounds in methanol and ethanol solutions were investigated. In this research, the authors identified the dual fluorescence of the anion, and supposed that the longwave fluorescence band is associated with a considerable charge delocalization between the tetrazole and phenyl ring, which is accompanied by a mutual twisting of the rings in the excited state.

In the present paper, electronic spectra and prototropic reactions in the ground and excited state in aqueous solutions are studied.

EXPERIMENTAL

The synthesis of *ortho-*, *meta-* and *para*-cyano-5-phenyltetrazole has been described elsewhere.[1] Aqueous solutions were obtained by dissolving the commercially available reagents. A Britton-Robinson buffer,[4] with variable ionic strength, was used from pH = 2 — 12. For pH = 3, the value nearest to the molecule-anion equilibrium constants (see Table II) ionic strength is 0.0143 mol.

Solutions more acidic than pH = 2 (to $H_o = -8$) were prepared by diluting the concentrated H_2SO_4 and acidity was expressed by the Hammett acidity function, generally defined by the equation:

$$H_o = -\log \frac{a_{H^+} f_B}{f_A} = pK_A - \log \frac{C_A}{C_B} \tag{1}$$

where a_{H^+} denotes hydrogen-ion activity, f_B and f_A molar-concentration activity coefficients and C_B and C_A concentrations of base and conjugate acid, respectively, of the particular class of chemically similar substances employed as indicators. pK_A is the thermodynamic ionization constant of conjugate acid. As it can be seen, in this case the activity coefficient correction is absorbed in H_o. In this work, H_o scale of Jorgenson and Hartter,[5] derived for primary amines, was used.

Measurements were carried out at about 24 °C in cells which were not thermostated.

The equilibrium constants in the ground state were calculated from spectrophotometric measurements and equations:

$$pK_1 = pH + \log \frac{A_B - A}{A - A_A} \tag{2}$$

$$pK_2 = H_o + \log \frac{A_B - A}{A - A_A} \tag{3}$$

where A_B and A_A are the absorbances, at a selected wavelength, of the base and conjugate acids, respectively, while A is the absorbance of the test solution of known pH (or H_o). The values for A_B and A_A were taken in the pH (or H_o) region, where absorbance was essentially constant, and they were at least two pH (or H_o) units above or below the pK value. The pK values listed in Table II are the mean values of several measurements at different wavelengths and for different test solutions.

The absorption spectra were measured on a »Zeiss« Model VSU 2 spectrophotometer, and the luminescence spectra on a Aminco-Bowman spectrophotofluorometer with an off-axis ellipsoid mirror condensing system. The luminescence spectra were corrected for the spectral response of the equipment.

RESULTS AND DISCUSSION

By examination of the absorption of cyano-5-phenyltetrazoles in aqueous solutions (pH 12 to $H_o = -8$), three different absorption spectra in the near UV spectral region were identified. In Figure 1, the absorption spectra of *ortho*-cyano-5-phenyltetrazole are given, which consists of three bands ($S_o \rightarrow S_1$, $S_o \rightarrow S_2$ and $S_o \rightarrow S_3$) of considerably different intensity. The spectrum with the positions of the band maxima 35100, 42000 and 48600 cm^{-1}, remains practically unchanged over the H_o range from about 0.8 to —2.5. By decreasing the acidity of the solvents, this spectrum transforms into a new spectrum shifted to a longer wavelength related to the former, and remains unchanged over the pH range 5—12. The dissociation constant $pK_1 = 2.9$ was determined spectrophotometrically, as described in the experimental section. Earlier,[1] using the potentiometric method, the thermodynamic constant for the molecule-anion equilibrium for ortho-cyano-5-phenyltetrazole was found to be 3.76 in a 50% ethanol-water mixture.

Consequently, we consider the above spectra to belong to the molecule and anion, and that the anion arises by deprotonation of the N—H group in the tetrazole ring in position 1, as it may be expected for the 5-phenyltetrazole derivative.[1]

The second transformation of the absorption spectrum of neutral *ortho*-cyano-5-phenyltetrazole appears by increasing the acidity of solvents from about $H_o = -2.5$ to —7. The new spectrum, batochromic shifted to that of the neutral form, we attribute to the protonated form (cation). We assume that protonation occurs at the nitrogen atom in the tetrazole ring in position
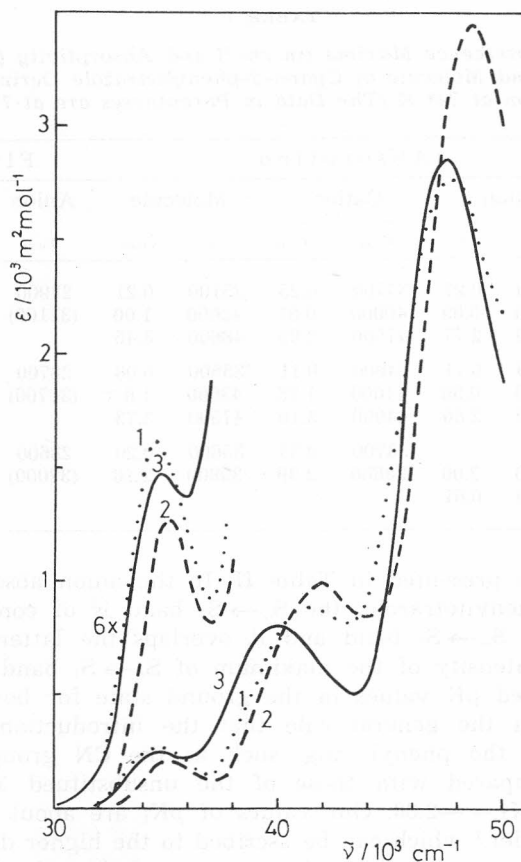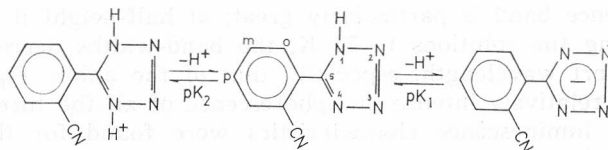
Figure 1. Absorption spectra of *ortho*-cyano-5-phenyltetrazole (10^{-4} mol/l) in aqueous solutions at room temperature: 1 — anion (pH = 6), 2 — molecule ($H_o = -0.1$) and 3 — cation ($H_o = -8$).

4, as it was established for tetrazole and some of its derivatives,[6,7] in the Hammett acidity region. Both processes can be depicted by the following Scheme:

The molecule-cation equilibrium constant $pK_2 = -4.7$ was determined spectrophotometrically. The protonation of cyano-5-phenyltetrazole had not been examined previously, while for the molecule-cation equilibrium of 5-phenyltetrazole —2.28 was obtained.[6]

Similar absorption characteristics were observed for *para*- and *meta*--derivatives. Summary data on the absorption spectra are listed in Table I,

TABLE I

Absorption and Fluorescence Maxima (in cm^{-1}) and Absorptivity (in 10^3 m^2/mol) for the Anion, Cation and Molecule of Cyano-5-phenyltetrazole Derivatives in Aqueous Solution at 298 K (The Data in Parentheses are at 77 K)

Position of cyano group	Absorption						Fluorescence		
	Anion		Cation		Molecule		Anion	Cation	Molecule
	ν_{max}	ε_{max}	ν_{max}	ε_{max}	ν_{max}	ε_{max}	ν_{max}	ν_{max}	ν_{max}
Ortho-	34500	0.27	34700	0.25	35100	0.21	27900	29300	30900
	41500	0.89	40000	0.81	42000	1.00	(31100)	(31000)	(32100)
	47600	2.77	47500	2.85	48600	3.45			
Meta-	35200	0.11	34800	0.11	35500	0.08	28700	30600	31900
	40000	0.99	41000	1.76	43000	1.6	(31700)	(31700)	(32600)
	46300	2.86	44000	3.10	47500	3.73			
Para-			33700	0.35	35600	0.20	28600	29400	32000
	38300	2.00	38600	2.39	39800	2.18	(32000)	(30100)	(32300)
	47500	0.61							

and pK values are presented in Table II. In the anion absorption spectrum of *para*-cyano-5-phenyltetrazole, the $S_o \rightarrow S_2$ band is of considerably higher intensity than the $S_o \rightarrow S_1$ band and it overlaps the latter, so neither the position nor the intensity of the maximum of $S_o \rightarrow S_1$ band could be determined. The obtained pK values in the ground state for both equilibria are in agreement with the general rule that the introduction of an electron acceptor group to the phenyl ring, such as the CN group, decreases the pK values as compared with those of the unsubstitued 5-phenyltetrazole, $pK_1 = 4.98$[1] and $pK_2 = -2.88$. Our values of pK_1 are about 20% lower than those obtained earlier,[1] which can be ascribed to the higher dielectric constant of water in relation to the dielectric constants of the solvent mixtures used in the cited work.

The fluorescence spectra of *meta*-cyano-5-phenyltetrazole at room temperature are shown in Figure 2. It is obvious that by dissociation or protonation of the molecule the red shift of the fluorescence spectrum is remarkably larger than that of the absorption spectrum. Especially large is the shift of the anion fluorescence spectrum in relation to that of the molecule, 3200 cm^{-1}, while the correspond shift of the cation spectrum is 1300 cm^{-1}. Besides, the width of the anion fluorescence band is particularly great; at half-height it is about 6000 cm^{-1}. By cooling the solutions to 77 K, the band-widths decrease and they shift to the short wavelength, especially that of the anion, Figure 3. There also appears a relatively intense phosphorescence of all the three dissociation forms. Similar luminescence characteristics were found for the other two derivatives (Table I).

The following two methods for determining excited singlet-state pK values, pK^*, are used:

a) Measurement of relative fluorescence intensity of the fluorescing species, as a function of pH (or H_o) — fluorometric titration;

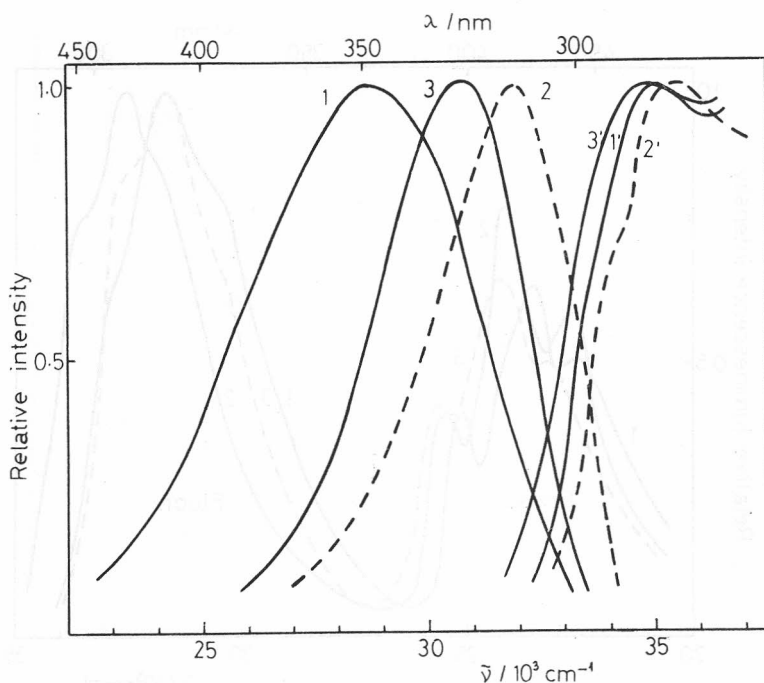b) Application of the Förster cycle:[8-11]

Figure 2. Fluorescence spectra (1, 2 and 3) and the longwave bands of absorption spectra (1', 2' and 3') of *meta*-cyano-5-phenyltetrazole (10^{-4} mol/l) in aqueous solutions at room temperature: 1 and 1' — anion (pH = 6), 2 and 2' — molecule ($H_o = -0.1$), and 3 and 3' — cation ($H_o = -7$).

$$pK^* = pK - 2.11 \cdot 10^{-3} \cdot (\tilde{\nu}^A_{0,0} - \tilde{\nu}^B_{0,0}) \qquad (4)$$

where $\tilde{\nu}^A_{0,0}$ and $\tilde{\nu}^B_{00,}$ are the wavenumber of the pure electronic transition in the acid and conjugate base, respectively. The 0,0 wavenumber for a species is estimated in the following ways:

b-1) The intersection point of the mutually normalized long-wave absorption band and the fluorescence band at 77 K;

b-2) The averaging absorption maximum and fluorescence maximum at 77 K;

b-3) The intersection point of the mutually normalized absorption and fluorescence band, as it was practised in the Förster laboratory;[12] and

b-4) The averaging of the absorption and fluorescence maxima.

Fluorometric titration of *meta*-cyano-5-phenyltetrazole is presented in Figure 4. From the values of pH (H_o), which correspond to the inflection points of the anion (A) and cation (C) fluoerscence titration curves, it is seen that the new anion-molecule and molecule-cation equilibria are established in the first excited state. In this way the excited-state pK values, $pK_1^* = 1.9$ and $pK_2^* = -3.9$, were obtained. These values show that this molecule, in the excited state, is a stronger acid and also a stronger base than in the ground state. The new anion-molecule equilibrium in the excited state is
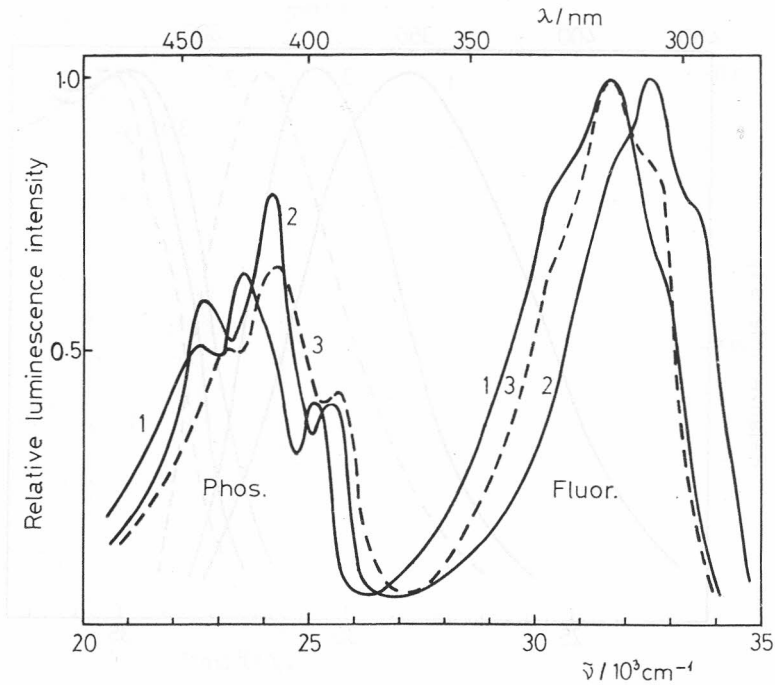
Figure 3. Luminescence spectra of *meta*-cyano-5-phenyltetrazole in aqueous solutions at 77 K: 1 — anion, 2 — molecule and 3 — cation.
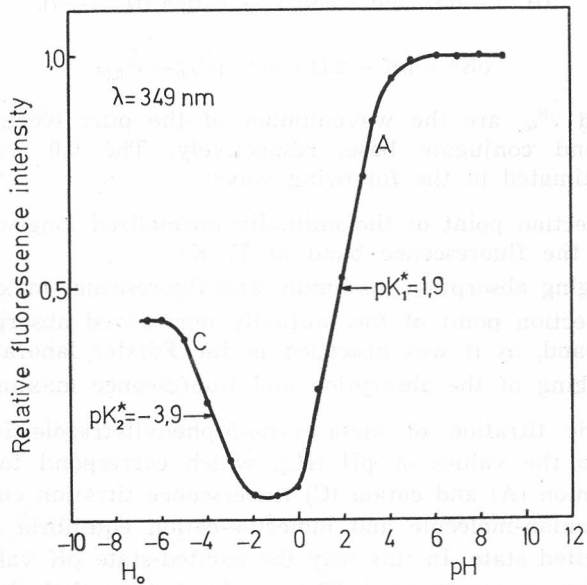

Figure 4. pH and Hammett acidity depedence of fluorescence intensity at $\lambda = 349$ nm of *meta*-cyano-5-phenyltetrazole (10^{-4} mol/l) in aqueous solutions at room temperature.

TABLE II

pK and pK* Values of Cyano-5-phenyltetrazole Derivatives Determined by
Different Methods

Position of cyano group	Ground state		Excited state		
	pK_1	pK_2	pK_1^*	pK_2^*	Method of calculation
Ortho-	2.9	—4.7	1.9		a
			1.4	—2.9	b-1
			1.2	—2.7	b-2
			1.3	—2.7	b-3
			—0.8	—2.6	b-4
Meta-	3.2	—5.4	1.9	—3.9	a
			1.5	—3.4	b-1
			1.8	—3.7	b-2
			1.7	—3.4	b-3
			—0.6	—3.6	b-4
Para-	3.1	—5.0	3.0		a
				—0.9	b-1
			(2.5)	—0.8	b-2
				—0.2	b-3
			(—4.1)	—0.4	b-4

also established for the *ortho*-derivative ($pK_1^* = 1.9$). For the *para*-derivative ($pK_1^* = 3.0$), the corresponding equilibrium is very close to that in the ground state; this result is confirmed by the other method.

Table II summarizes all the excited-state pK values obtained by both methods. It is seen, that both methods gave the same results for the pK_2^* for all the compounds, though some dispersal of values is present. The average values of pK_2^* for the *ortho-* *meta-* and *para*-derivative are about —2.7, —3.6 and —0.65, respectively. Apparent pK_2^* values are unaffected by the solvent and configurational relaxation process, but are affected by the position of the substituent.

pK_1^* values for the *para*-derivative were calculated by the Förster cycle entirely from the fluorescence spectra, because the $S_o \rightarrow S_1$ absorption band of the anion, as mentioned above, could not be identified (values in parentheses, Table II). In this way the obtained value $pK_1^* = 2.5$, in correlation with the pK_1^* values for *ortho-* and *meta*-substituent, suggests that the value 3.0 obtained by fluorometric titration, represents the pK_1^*. This means that the anion-molecule equilibrium in the excited state is only slightly different from that in the ground state.

Comparing the pK_1^* values listed in Table II, it can be seen that there is considerable disagreement between the values obtained by method b-4 and the other values for the same compound. It is the consequence of a remarkable Stokes shift of the maximum of the anion fluorescence spectrum at room temperature. The enormous difference in the positions of the maximum of anion fluorescence spectrum at room temperature and the fluorescence maximum at low temperature may be ascribed to the structural rearrangement of the anion in the excited state. We accept the supposition[2] that the charge transfer from the tetrazole ring to the phenyl ring in the

excited state of the anion, owing to the electron-acceptor character of the CN group, is accompanied by a mutual twisting of the rings. As a result, a new, so-called, twisted internal charge transfer (TICT) excited state[13,14] of a markedly lower energy is formed, and the fluorescence occurring from it is red shifted in relation to that of the untwisted species, which appears at low temperature as only one. The broad band of anion fluorescence which appears at room temperature in aqueous solutions represents the super-positions of the fluorescence bands which originate from the twisted and untwisted species, and its maximum is between the positions of the maxima of the superposed bands. In this case the 0,0 transition obtained from the intersection of the fluorescence and absorption spectra (method b-3) differs considerably from 0,0 transition obtained by averaging the maximum of this complex fluorescence spectrum and the maximum of the anion absorption band (method b-4), Figure 2, and, consequently a large discrepancy of the correspondingly calculaetd pK_1^* values is present.

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SAŽETAK

Elektronski spektri cijano-5-feniltetrazola

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Izmereni su apsorpcioni i luminescentni spektri orto-, meta- i para-ciano-5--feniltetrazola u vodenim rastvorima na sobnoj i niskoj temperaturi. Ispitivanja su vršena u sredinama od super-kiselih ($H_o = -8$) do baznih (pH = 12). Utvrđene su tri forme disocijacije: anjon, molekul i katjon. Spektrofotometrijski su određene odgovarajuće konstante ravnoteže u osnovnom stanju, dok su u prvom pobuđenom singletnom stanju eksperimentalno određene iz titracijskih krivih, a računski pomoću Förster-ova ciklusa.