

INFLUENCE OF COMPLEXING AND EXCITATION ENERGY ON SPECTRAL AND LUMINESCENT PROPERTIES OF 2-AMINO-4-METHYLPHENOL

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Energy level diagrams of 2-amino-4-methylphenol and its complexes with water are calculated by the method of intermediate neglect of differential overlap (INDO). It is demonstrated that the substitution by the amino group results in the dependence of the quantum fluorescence yield on the excitation energy. The decrease of the quantum fluorescence yield of 2-amino-4-methylphenol in going from hexane to water is explained. Complexing of the 2-amino-4-methylphenol molecule with water with the formation of the H-bond reduces the quantum fluorescence yield compared to the isolated molecule due to the increased efficiency of the $S_1 \rightarrow T_4$ conversion.

INTRODUCTION

Interest in the study of spectral, luminescent, and photochemical properties of methyl-substituted phenols is explained not only by an acuteness of environmental problems (methyl-substituted phenols are widespread phenol pollutants [1, 2]) but also by the increased necessity of studying the properties of amino acids incorporating them [3, 4]. The methyl groups influence the electronic spectrum of phenol, causing the shift of electronic transitions toward longer wavelengths, little changes of the oscillator forces, and the formation of the $S_0 \rightarrow S_2(\pi\sigma^*)$ transition with participation of the C-CH₃ bond [5]. Substitution by the methyl group has no noticeable influence on the energy of states, photophysical processes, and quantum fluorescence yield. Bazyl' *et al.* [5] have demonstrated experimentally that the substitution of the hydrogen atom by the methyl group in *para*-position in phenol results in the dependence of the quantum fluorescence yield on the excitation energy. The quantum-chemical calculations carried out in [6] demonstrated that this dependence was caused by a more efficient occupation of photodissociative states under short-wavelength excitation and hence by a more efficient breaking of the OH bond. Irrespective of the excitation energy, the photolysis of isolated molecules and complexes is most efficient in the triplet photodissociative state. The larger photolysis quantum yield of 4-methylphenol under short-wavelength excitation is caused not only by the higher efficiency of occupation of photodissociative states but also by the smaller energy of photoreaction activation.

The present work studies the influence of substitution by the amino group, complexing, and excitation energy on the spectral and luminescent properties of 4-methylphenol.

1. METHODS OF INVESTIGATION

Quantum-chemical calculations of the 2-amino-4-methylphenol molecule and its complexes with water were performed by the method of intermediate neglect of differential overlap (INDO) with parameterization [7]. The wave functions obtained were used to calculate the excited electronic state energies and rate constants of the photophysical processes according to [8–10]. The theoretical quantum yield was calculated from the formula

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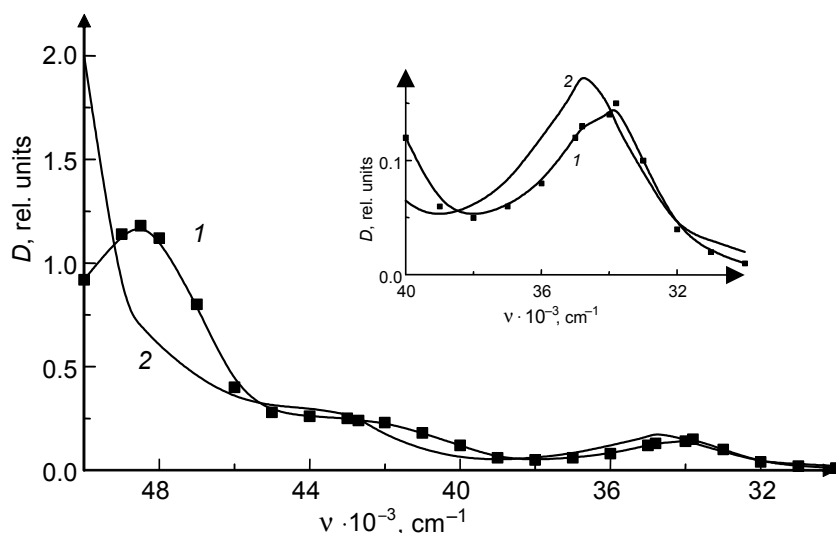


Fig. 1. Absorption spectrum of 2-amino-4-methylphenol in hexane (curve 1) and water (curve 2).

$$\gamma = k_r / (k_r + k_{ic} + k_{ST}),$$

where k_r , k_{ic} , and k_{ST} are the rate constants of the radiative decomposition and internal and intercombination conversion processes. The method of molecular electrostatic potential was used to determine the spatial structure of the H-bonded complexes and changes in intermolecular interactions under electronic excitation [11].

In quantum-chemical calculations of 2-amino-4-methylphenol and its complexes with water, the geometry of water and 2-amino-4-methylphenol molecules was borrowed from [12, 13], with the distances in complexes $R_{OH...O} = 1.74 \text{ \AA}$, $R_{O...O} = 2.8 \text{ \AA}$, and $R_{O...N} = 2.96 \text{ \AA}$. They correspond to the weak hydrogen bond between the 2-amino-4-methylphenol and water molecules.

The experimental absorption and fluorescence spectra of 2-amino-4-methylphenol with concentration of 10^{-4} M in water and hexane were registered with Specord M40 and Hitachi 850 spectrophotometers using the standard procedure. The quantum fluorescence yield was determined experimentally by the relative method described in [14]. The measurement error was 10–15%. The phenol solution in water with the quantum fluorescence yield equal to $\gamma = 0.22$ [15] and well investigated spectral and luminescent properties [16, 17] was used as an etalon.

2. DISCUSSION OF RESULTS

Figure 1 shows experimental spectra of 2-amino-4-methylphenol in water and hexane. From the figure it can be seen that the absorption band maxima of the 2-amino-4-methylphenol molecule in water are shifted toward shorter wavelengths compared to the spectrum in hexane. In going from the nonpolar to polar solvent, the quantum fluorescence yield of 2-amino-4-methylphenol decreases from $\gamma = 0.14$ in hexane to $\gamma < 10^{-3}$ in water.

Calculations of the molecular electrostatic potentials demonstrated that the H-bond of 2-amino-4-methylphenol in the ground state with water molecules was formed both by the oxygen atom of the OH group and by the nitrogen atom of the NH_2 group (the energy minima of the molecular electrostatic potential were 255 and 183 kJ/mole, respectively). Moreover, the H-bond was first formed by oxygen and then by nitrogen. In both cases, spatial configurations of the complex were nonplanar. Complexing of this type causes the energy of electron transitions at which absorption occurs in these wavelength ranges to increase.

TABLE 1. Calculated Absorption Spectrum of the 2-Amino-4-Methylphenol Molecule and Its Complex with Water Molecules

State	Isolated molecule			State	Complex		
	E_i, cm^{-1}	f	Nature of states		E_i, cm^{-1}	f	Nature of states
$S_1(\pi\pi^*)$	33800	0.06	$0,9 24 \rightarrow 25\rangle,$ $0,4 23 \rightarrow 26\rangle$	$S_1(\pi\pi^*)$	34300	0.06	$0,9 32 \rightarrow 33\rangle,$ $0,4 31 \rightarrow 34\rangle$
$S_2(\pi\pi^*)$	39300	0.19	$0,9 24 \rightarrow 26\rangle,$ $0,3 23 \rightarrow 25\rangle$	$S_2(\pi\pi^*)$	40400	0.18	$0,9 32 \rightarrow 34\rangle,$ $0,3 31 \rightarrow 33\rangle$
$S_3(\pi\sigma^*)$	40700	0.00	$0,5 24 \rightarrow 27\rangle$	$S_3(\pi\sigma^*)$	40800	0.01	$0,7 32 \rightarrow 35\rangle,$ $0,6 32 \rightarrow 36\rangle,$ $0,4 32 \rightarrow 37\rangle$
$S_4(\pi\sigma^*)$	41750	0.00	$0,4 24 \rightarrow 27\rangle,$ $0,9 24 \rightarrow 29\rangle$	$S_4(\pi\pi^*)$	42070	0.01	$0,7 32 \rightarrow 35\rangle,$ $0,5 32 \rightarrow 36\rangle,$ $0,3 32 \rightarrow 37\rangle$
$S_5(\pi\sigma^*)$	44600	0.00	$0,6 23 \rightarrow 27\rangle$	$S_5(\pi\sigma^*)$	44500	0.00	$0,7 32 \rightarrow 36\rangle,$ $0,4 32 \rightarrow 37\rangle,$ $0,4 31 \rightarrow 35\rangle$
$S_6(\pi\pi^*)$	45900			$S_6(\pi\pi^*)$	46170		
$S_7(\pi\pi^*)$	47500	0.85	$0,4 24 \rightarrow 25\rangle,$ $0,4 23 \rightarrow 25\rangle,$ $0,7 23 \rightarrow 26\rangle$	$S_7(\pi\pi^*)$	48200	0.8	$0,5 32 \rightarrow 33\rangle,$ $0,8 31 \rightarrow 34\rangle$

Notes. Here E_i is the energy and f is the oscillator force of the electronic transition.

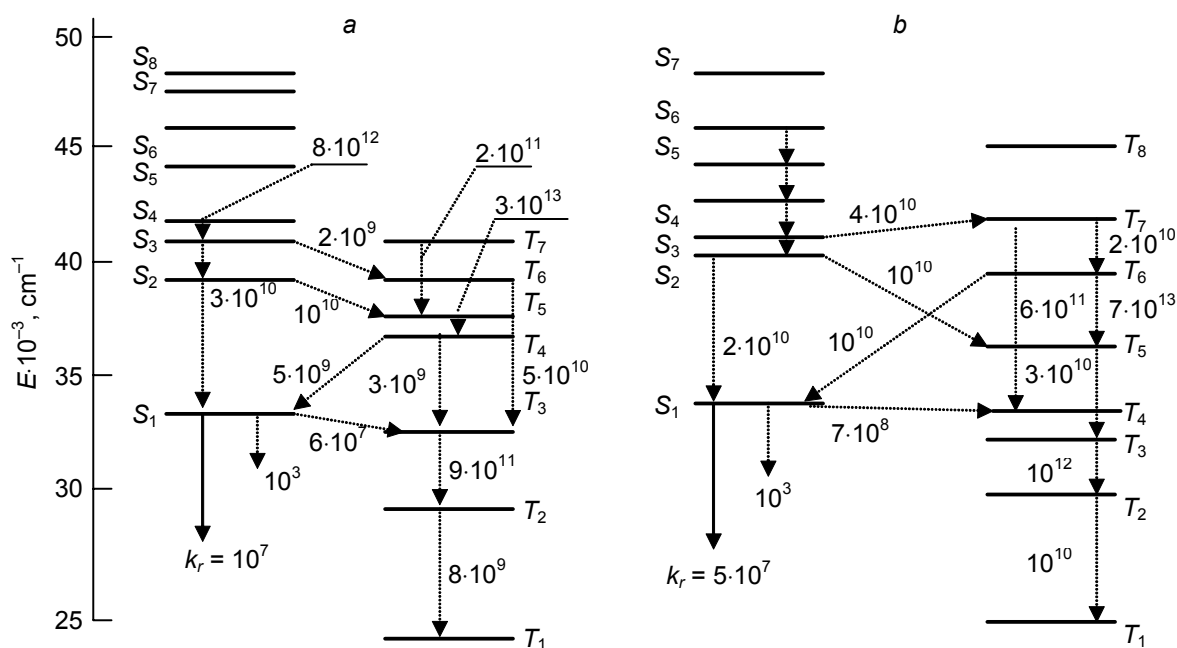


Fig. 2. Energy level diagram of electronically-excited states of 2-amino-4-methylphenol (a) and its complexes (b). Dotted arrows indicate the most significant nonradiative processes, and the numbers adjacent to them indicate the rate constants of these processes, in s^{-1} .

Figure 2 and Table 1 illustrate the energy level diagram of electronically-excited states of the isolated 2-amino-4-methylphenol molecule and its complex with water molecules in the 1:2 ratio. The calculated spectrum of electronic states

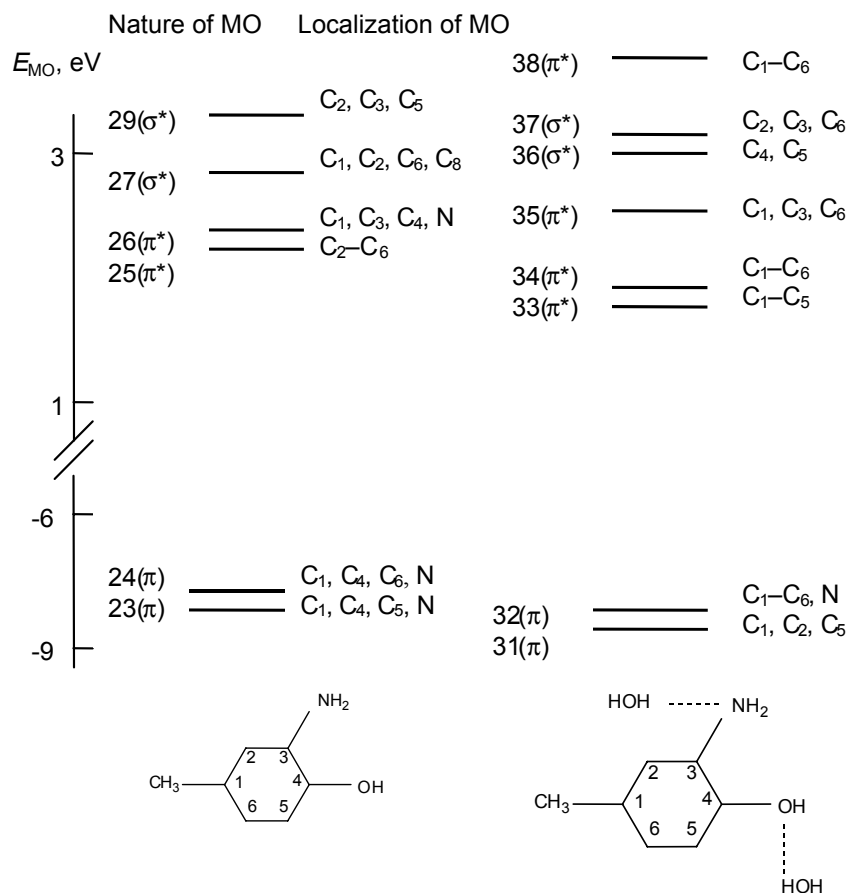


Fig. 3. Nature and localization of molecular orbitals in 2-amino-4-methylphenol and its complex with water.

of the isolated molecule should be compared with the experimental spectrum in the gas phase or in an inert solvent (hexane). A comparison of the calculated results (Table 1) and experimental spectra (Fig. 1) in hexane and water demonstrates their good agreement. The NH₂ group in 4-methylphenol causes the following changes. Three absorption bands with maxima at ~34000, 42000, and 48000 cm⁻¹ are detected in the absorption spectra of 2-amino-4-methylphenol at frequencies up to ~50000 cm⁻¹. The results of calculations demonstrate that the long-wavelength absorption band in the spectra is formed by the $S_0 \rightarrow S_1(\pi\pi^*)$ electronic transition (Table 1). The absorption bands in the middle and short-wavelength ranges of the spectrum are formed by several transitions of various orbital nature (Fig. 3); however, the intensity of absorption in these ranges is determined mainly by the $S_0 \rightarrow S_2(\pi\pi^*)$ (the band centered at 42000 cm⁻¹), $S_0 \rightarrow S_7(\pi\pi^*)$, and $S_0 \rightarrow S_8(\pi\pi^*)$ transitions (the band centered at 48000 cm⁻¹). The amounts of decrease in the energy of electronic transitions into the S_2 and S_3 states of 4-methylphenol that determine the absorption in the middle range of the spectrum differ, and the inversion of energy levels is observed in the 2-amino-4-methylphenol molecule (Table 2). An analysis of the nature of molecular orbitals (MO) participating in the formation of the wave functions of excited electronic states (Fig. 3) demonstrate that no σ^* -type MO are formed with participation of the O...H bond of the molecule in these ranges of the spectrum. The σ^* -type orbital of the $S_3(\pi\sigma^*)$ and $T_4(\pi\sigma^*)$ states is localized mainly on the C...N and C...CH₃ bonds of the aromatic fragment. Electronic transitions of the isolated 2-amino-4-methylphenol molecule from the ground state to the $S_1(\pi\pi^*)$ and $S_2(\pi\pi^*)$ excited states are accompanied by the electronic density transfer mainly from the OH and NH₂ groups to carbon atoms of the aromatic ring (Table 3). Redistribution of the electronic density, in turn, must result in a noticeable reorganization of the solvate shell of the molecule in the solution under excitation.

TABLE 2. Calculated Absorption Spectrum of the 4-Methylphenol Molecule and Its Complex with Water Molecules [5]

State	Isolated molecule		Complex	
	E_i, cm^{-1}	f	E_i, cm^{-1}	f
$S_1(\pi\pi^*)$	36300	0.06	36560	0.05
$S_2(\pi\sigma^*)$	42438	0.00	42739	0.00
$S_3(\pi\pi^*)$	43332	0.20	43560	0.20
$T_1(\pi\pi^*)$	27860	–	28061	–
$T_2(\pi\pi^*)$	35120	–	35222	–
$T_3(\pi\pi^*)$	36322	–	36343	–

Notes. Here E_i is the energy and f is the oscillator force of the electronic transition.

TABLE 3. Changes in the Effective Charge of Fragments of the Phenol Molecule and Its Substitutes and Their Complexes with Water under Electronic Excitation

Fragment of the molecule	Isolated molecule			Complex with water		
	S_1	S_2	S_3	S_1	S_2	S_3
Phenol						
Phenol ring	0.089	0.103	0.087	0.104	0.105	0.099
OH group	-0.090	-0.103	-0.134	-0.104	-0.105	-0.148
4-methylphenol						
Phenol ring	0.121	0.111	0.005	0.132	0.120	0.007
OH group	-0.088	-0.082	-0.130	-0.101	-0.095	-0.146
CH ₃ group	-0.033	-0.029	0.125	-0.031	-0.025	0.139
2-amino-4-methylphenol						
Phenol ring	0.206	0.207	0.068	0.232	0.231	0.207
OH group	-0.073	-0.075	0.006	-0.049	-0.054	-0.057
CH ₃ group	-0.007	0.0	0.048	-0.013	-0.006	0.052
NH ₂ group	-0.126	-0.132	-0.123	-0.165	-0.167	-0.197

Notes. The plus sign means an increase in the effective electronic charge of the fragment, and the minus sign means a decrease in the effective electronic charge of the fragment.

From Table 3 it can be seen that substitutes incorporated into the aromatic ring of the phenol molecule increase the charge transferred during the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transitions. The most efficient charge transfer is observed for 2-amino-4-methylphenol excited into the S_1 and S_2 states. Redistribution of the electronic density is the reason for changing the minima of the molecular electrostatic potential during excitation and complexing.

The H-bond formed by oxygen and nitrogen atoms of 2-amino-4-methylphenol with water molecules leads to the fact that electronic transitions from the ground to the excited level are accompanied by the electronic density transfer mainly from the amino group to carbon atoms of the aromatic ring in positions 2 and 5 (Table 3). Under excitation, the proton acceptor ability of oxygen and nitrogen atoms sharply decreases (the minima of the molecular electrostatic potential are -62 and -52 kJ/mole, respectively) and a minimum of the molecular electrostatic potential is formed above the aromatic ring plane of the molecule (the minimum molecular electrostatic potential is 109 kJ/mole). These changes in the proton acceptor abilities of oxygen and nitrogen atom lead to weakening of the H-bonds with these centers and their intermolecular interaction with the phenol ring. In other words, considerable reorganization of the solvate shell of 2-amino-4-methylphenol molecules in the $S_1(\pi\pi^*)$ state compared to the ground state are expected.

The basic channel of fluorescent state deactivation, as for phenol and *para*-cresol molecules and their complexes with water [6], is the singlet-triplet conversion in the $S_1(\pi\pi^*) \rightarrow T_3(\pi\pi^*)$ (isolated molecule) and $S_1(\pi\pi^*) \rightarrow T_4(\pi\pi^*)$ channels (complex). Substitution by the amino group in *para*-cresol changes the efficiency of radiative and nonradiative decomposition channels and decreases the quantum fluorescence yield of the isolated molecule (Fig. 2). The relationship among the probabilities of energy deactivation of the $S_1(\pi\pi^*)$ state in different channels results in the fluorescence of 2-amino-4-methylphenol and its complex with water with quantum yield $\gamma = 0.14\text{--}0.008$, which is in agreement with the available experimental data. For the excitation of the isolated molecule into the S_1 state, the main deactivation channel will be the intercombination conversion in the $S_1(\pi\pi^*) \rightarrow T_3(\pi\pi^*)$ channel (Fig. 2). Excitation in the middle range of the absorption spectrum (the $S_0 \rightarrow S_2$ transition) results in a partial loss of absorption energy in the channel of triplet states, because the probabilities of the $S_2 \rightarrow S_1$ and $S_2 \rightarrow T_5$ processes are close in values as well as the probabilities of $T_4 \rightarrow S_1$ and $T_4 \rightarrow T_3$ conversions. This will lead to the dependence of the quantum fluorescence yield on the excitation energy. Complexing strengthens considerably this dependence. Under excitation into the S_2 state, the competition between the $S_2 \rightarrow S_1$ and $S_2 \rightarrow T_5$ processes takes place (Fig. 2). A portion of the excitation energy, deactivating in the triplet state channel by the $S_2(\pi\pi^*) \rightarrow T_5(\pi\sigma^*)$ conversion, is transferred to the $T_1(\pi\pi^*)$ state due to the high rate of the $T_4 \rightarrow T_3 \rightarrow T_2$ internal conversion and lower conversion rate in the $T_5 \rightarrow T_4$ channel. Thus, the incorporation of the amino group into the 4-methylphenol molecule and complexing with hydrogen bonds even in the absence of photochemical reactions must result in a noticeable dependence of the quantum fluorescence yield on the excitation energy.

In summary, we can conclude the following:

1. Substitution of 4-methylphenol by the amino group results in the shift of the absorption bands toward longer wavelengths and the decrease of the quantum fluorescence yield.
2. The deactivation energy of the S_1 state under excitation into the long-wavelength absorption band of the isolated 2-amino-4-methylphenol molecule is determined by the competition between the radiative decomposition ($k_r = 10^7 \text{ s}^{-1}$) and intercombination conversion processes ($k_{ST} = 6 \cdot 10^7 \text{ s}^{-1}$).
3. Complexing with water results in the shift of the absorption bands toward shorter wavelengths compared to the isolated 2-amino-4-methylphenol molecule, change of the proton acceptor center of the molecule under excitation into the S_1 state, and strengthening of the dependence of the quantum fluorescence yield on the excitation energy.

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